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Assessment of Technology for Control of Toxic Effluents from the Electric Utility Industry

Radian Corp, Austin, Tex

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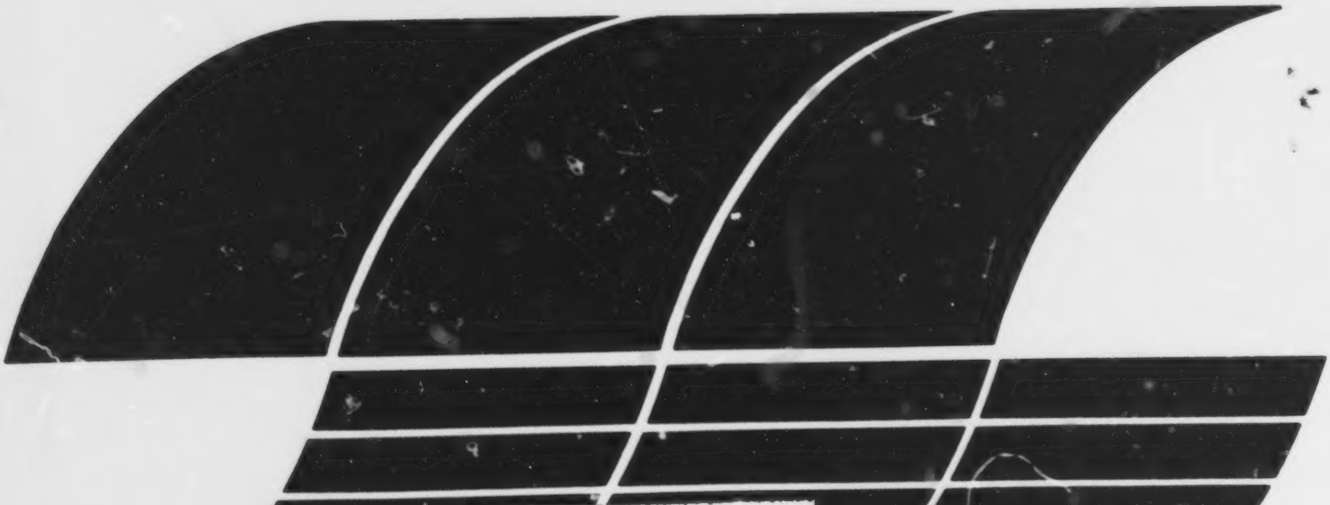

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J.D. Colley, C.A. Muela, M.L. Owen,
N.P. Meserole, J.B. Riggs, and J.C. Terry

Radian Corporation
8500 Shoal Creek Boulevard
Austin, Texas 78766

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EPA Project Officer: Julian W. Jones

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
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SECTION 1

INTRODUCTION

Effluent guidelines, including new source performance standards (NSPS) for the steam-electric power generating industry were first published in 1974. Discharge limits to be met by July of 1983 (as required in the 1972 Federal Water Pollution Control Act) were established as those attainable by the best available technology economically achieavble (BATEA). The NSPS were based upon best available demonstrated technology. The BATEA and NSPS limits, which are summarized in Table 1-1, are currently undergoing comprehensive review by the EPA (RI-160).

The EPA review will focus primarily on regulation of priority pollutants. More specifically, this will include the 129 "unambiguous" chemicals listed in Table 1-2 (RI-160). Based on preliminary EPA findings, the pollutants in this list which are most likely to be present in utility effluents are indicated by an asterisk.

The EPA has iniciated a three-pronged effort to develop background information to support the establishment of effluent standards for priority pollutants. The objectives of this effort are (1) identification and quantification of priority pollutants in utility discharges, (2) identification and assessment of existing control technologies applicable to the control of those pollutants, and (3) detailed economic analyses of the costs of applying the identified control technologies to utility industry wastewater streams. This report presents the results of a study which concentrated on the second of the aforementioned tasks.

More specifically, this study was intended to assist EPA's Effluent Guidelines Division in identifying and assessing potential priority pollutant control technologies. The specific objectives of the study included:

- Identification of available technologies used by utilities or related industries to control priority pollutants,

TABLE 1-1. DISCHARGE LIMITS FOR THE UTILITY INDUSTRY[1, 2]

Stream Pollutant	BPCTCA limit, mg/l Max[3]	BPCTCA limit, mg/l Avg[4]	BATEA limit, mg/l Max[3]	BATEA limit, mg/l Avg[4]	Limit for new sources, mg/l Max[3]	Limit for new sources, mg/l Avg[4]
All streams						
pH (except once-through cooling	6.0-9.0		6.0-9.0		6.0-9.0	
PCBs	No Discharge		No Discharge		No Discharge	
Low-volume waste streams						
TSS	100	30	100	30	100	30
Oil and grease	20	15	20	15	20	15
Bottom-ash transport water						
TSS	100	30	100[5]	30[5]	100[6]	30[6]
Oil and grease	20	15	20[5]	15[5]	20[6]	15[6]
Fly ash transport water						
TSS	100	30	100	30	No Discharge	
Oil and grease	20	15	20	15	No Discharge	
Metal-cleaning wastes						
TSS	100	30	100	30	100	30
Oil and grease	20	15	20	15	20	15
Copper (total)	1	1	1	1	1	1
Iron (total)	1	1	1	1	1	1
Boiler blowdown						
TSS	100	30	100	30	100	30
Oil and grease	20	15	20	15	20	15
Copper (total)	1	1	1	1	1	1
Iron (total)	1	1	1	1	1	1
Once-through cooling water						
Free available chlorine[7]	0.5	0.2	0.5	0.2	0.5	0.2
Cooling tower blowdown						
Free available chlorine[7]	0.5	0.2	0.5	0.2	0.5	0.2
Zinc[9]			1	1		
Chromium[9]			0.2	0.2		
Phosphorus[9]			5	5		
Other corrosion inhibitors	Limits determined on a case-by-case basis					
Material-storage runoff[8]						
TSS	50		50		50	
pH	6.0-9.0		6.0-9.0		6.0-9.0	

---

[1] Except where specified otherwise, allowable discharge equals flow multiplied by concentration limitation. Where waste streams from various sources are combined for treatment or discharge, quantities of each pollutant attributable to each waste source shall not exceed the specified limitation for that source.

[2] All sources must meet State Water Quality Standards by 1977 (Section 301 (b)(1)(c)).

[3] Maximum for any one day.

[4] Average of daily values for 30 consecutive days.

[5] Allowable discharge equals flow multiplied by concentration divided by 12.5.

[6] Allowable discharge equals flow multiplied by concentration divided by 20.0.

[7] Limits given are maximum and average concentrations. Neither free available chlorine nor total residual chlorine may be discharged from any unit for more than 2 hr in one day; not more than one unit of any plant may discharge free available or total residual chlorine at the same time, unless the utility can demonstrate that the units in a particular location cannot operate at or below this level of chlorination.

[8] Only runoff flow from material-storage piles associated with the reference 10-yr, 24-hr rainfall is exempt from these limitations.

[9] Not applicable for BPCTCA, no detectable discharge from new sources.

Source: RI-160

TABLE 1-2. LIST OF PRIORITY POLLUTANTS

Acenaphthene
* Acrolein
Acrylonitrile
* Benzene
Benzidine
* Carbon tetrachloride (tetrachloromethane)
* Chlorobenzene
* 1,2,4-Trichlorobenzene
* Hexachlorobenzene
* 1,2-Dichloroethane
* 1,1,1-Trichloroethane
* Hexachloroethane
* 1,1-Dichloroethane
* 1,1,2-Trichloroethane
* 1,1,2-Tetrachloroethane
* Chloroethane
* Bis(chloromethyl) ether
* Bis(2-chloroethyl) ether
* 2-Chloroethyl vinyl ether (mixed)
2-Chlorohaphthalene
* 2,4,6-Trichlorophenol
4-Chloro-m-cresol
* Chloroform (trichloromethane)
* 2-Chlorophenol
* 1,2-Dichlorobenzene
* 1,3-Dichlorobenzene
* 1,4-Dichlorobenzene
3,3-Dichlorobenzidine
1,1-Dichloroethylene
1,1-Trans-dichloroethylene
* 2,4-Dichlorophenol
1,2-Dichloropropane
1,3-Dichloropropylene (1,3-Dichloropropene
2,4-Dimethylphenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
1,2-Diphenylhydrazine
Ethylbenzene
Fluoranthene
4-Chlorophenylphenyl ether
4-Bromophenylphenyl ether
Bis-(2-chloroisopropyl) ether
Bis(2-chloroethoxy) methane
Methylene chloride (dichloromethane)
Methyl chloride (chloromethane)

Methyl bromide (bromomethane)
Bromoform (tribromomethane)
Dichlorobromomethane
Trichlorofluoromethane
Dichlorodifluoromethane
Chlorodibromomethane
Hexachlorobutadiene
Hexachlorocyclopentadiene
Isophorene
* Naphthalene
Nitrobenzene
2-Nitrophenol
4-Nitrophenol
2,4-Dinitrophenol
4,6-Dinitro-o-cresol
* N-nitrosodimethylamine
* N-nitrosodiphenylamine
* N-nitrosodi-n-propylamine
* Pentachlorophenol
* Phenol
Bis(2-ethylhexyl) phthalate
Butylbenzyl phthalate
Di-n-butyl phthalate
Diethyl phthalate
Dimethyl phthalate
1,2-Benzanthracene
3,4-Benzopyrene
3,4-Benzofluoranthene
11,12-Benzofluoranthene
Chrysene
Acenaphthylene
* Anthracene
1,12-Benzoperylene
Fluorene
* Phenanthrene
1,2,5,6-Dibenznathracene
Indeno(1,2,3-c,d) pyrene
Pyrene
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)
Tetrachloroethylene
* Toluene
Trichloroethylene
Vinyl chloride (chloroethylene
Aldrin
Dieldrin
Chlordane (technical mixture and metalbolites)

4,4´-DDT
4,4´-DDE (p,p´-DDX)
4,4´-DDD (p,p´- TDE)
α-Endosulfan
β-Endosulfan
Endosulfan sulfate
Endrin
Endrin aldehyde
Endrin ketone
Heptachlor
Heptachlor epoxide
α-Hexachlorocyclohexane
β-Hexachlorocyclohexane
γ-Hexachlorocyclohexane (lindane)
δ-Hexachlorocyclohexane
* Polychlorinated biphenyl (Arochlor 1016)
* Polychlorinated biphenyl (Arochlor 1221)
* Polychlorinated biphenyl (Arochlor 1232)
* Polychlorinated biphenyl (Arochlor 1242)
* Polychlorinated biphenyl (Arochlor 1248)
* Polychlorinated biphenyl (Arochlor 1254)
* Polychlorinated biphenyl (Arochlor 1260)
Toxaphene
* Antimony (total)
* Arsenic (total)
* Asbestos (fibro)
* Beryllium (total)
* Cadmium (total)
* Chromium (total)
* Copper (total)
* Cyanide (total)
* Lead (total)
* Mercury (total)
* Nickel (total)
* Selenium
* Silver (total)
* Thallium (total)
* Zinc (total)

---

* Substances most likely to be present in utility effluents based on preliminary data and literature survey.

SOURCE: RI-160, preliminary EPA data.

- Preliminary assessment of the identified technologies to select those which appear to be the most applicable to the utility industry, and

- Detailed assessment of the potential effectiveness and economics of each selected process in a utility application.

Throughout the performance of the task, primary emphasis was placed on the identification and assessment of control technologies which are currently used or available commercially. Technologies in the research and development stage received secondary emphasis, particularly in cases where detailed or reliable information on performance and cost was not available.

The results of the effort to identify and quantify the priority pollutants (Objective 1 - as described above) were not available for this assessment of control technology effectiveness. As a result since discharge limits for priority pollutants have not been identified, it was not possible to address the feasibility of meeting specific effluent limits by applying the treatment technologies considered to specific levels of pollutants. With these limitations in mind, the question of what pollutants to address was based on the preliminary EPA list shown in Table 1-2. Applicable control processes and potential control levels for these pollutants were quantified to the maximum extent possible.

SECTION 2

RESULTS AND CONCLUSIONS

A brief summary of the results of the study is presented in this section. Section 5, Assessment of Selected Control Technologies contains a more indepth discussion of the results.

Wastewater control technologies potentially applicable to the utility industry were surveyed and the most promising control processes were selected for more intensive review. These processes are listed in Table 2-1 along with a qualitative assessment of priority pollutant removal potential of each. This table addresses only the question of removal potential because the specific performance achieved in a given application will depend upon the concentrations of the effected species as well as the physical characteristics of the treatment system and the stream(s) treated.

Detailed evaluations of the treatment processes listed in Table 2-1 were made as part of this study. These evaluations involved comparing the processes with respect to their:

- estimated priority pollutant control capabilities
- energy requirements
- secondary pollutant emission problems
- capital and operating costs

The results of this comparative analysis are summarized in Table 2-2.

The priority pollutant removal estimates which are shown in Table 2-2 were based for the most part on performance data derived from industries other than the utility industry. The cost data reported are based upon designs for 200,000 gal/day treatment systems.

TABLE 2-1. PRIORITY POLLUTANTS POTENTIALLY CONTROLLED BY SELECTED TECHNOLOGIES

	CLASSES OF PRIORITY POLLUTANTS CONTROLLED																												
PROCESS	Acrolein	Antimony & Compounds	Arsenic & Compounds	Benzene	Beryllium & Compounds	Cadmium & Compounds	Carbon Tetrachloride	Chlorinated Benzenes	Chlorinated Ethanes	Chloroalkyl Ethers	Chlorinated Phenols	Chloroform	Chromium & Compounds	Copper & Compounds	Cyanides	2,4-Dichlorophenol	Lead & Compounds	Mercury & Compounds	Napthalene	Nickel & Compounds	Nitrosamines	Pentachlorophenol	Polychlorinated Biphenyls	Polynuclear Aromatic Hydrocarbons	Selenium & Compounds	Silver & Compounds	Thallium & Compounds	Toluene	Zinc & Compounds
ACTIVATED CARBON	✓		*	✓	*		✓	✓	✓	✓	✓	✓	*		*	✓			✓			✓	✓	✓	*				*
LIME PRECIPITATION		✓	✓			✓							✓	✓			✓	✓		✓						✓	✓		✓
REVERSE OSMOSIS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
VAPOR COMPRESSION DISTILLATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
EVAPORATION PONDS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
* Highly site-specific																													

TABLE 2-2. COMPARISON OF CONTROL TECHNOLOGIES

Control Technology	Projected Effectiveness	Estimated Energy Requirements (kW-hr/1000 gal)	Sources of Secondary Emissions Air	Sources of Secondary Emissions Water	Sources of Secondary Emissions Solid	Estimated Costs□ Capital ($$10^6$)	Estimated Costs□ Operating $/1000 gal
Activated Carbon	Good removal (80-99%) of aromatics; poor removal efficiency for heavy metals	.35	From regeneration step	Quench water	Spent carbon if no regeneration is used	.25	.10
Lime Precipitation	Good for removal of heavy metals Residual concentrations for most metals are less than .1 ppm	8	---	Liquid occluded with solid sludge	Sludge produced from precipitation	.9	1.0
Reverse Osmosis	90-98% rejection of dissolved solids; 95% removal of organics; 75% water recovery	8-10	---	Concentrated brine and membrane backwash	---	.3	.75
Vapor Compression Distillation	99.9% salt rejection; 90% water recovery	80-100	Vent from aerator	Concentrated brine slurry	Solids in concentrated slurry	2.0	1.9
Evaporation Ponds	Seepage is the only liquid discharge from evaporation ponds and is dependent upon the type of pond and liner.	.3-.5	Evaporation of organics in the feed water	Seepage	Precipitation products produced in pond	1.6Δ	1.6Δ
Graded Media Filter	Removes suspended solids in the particle size range of .1 to 50μ.	.3	---	Filter backwash	Solids in filter backwash	.07	.12
Solid Waste Disposal by Landfill	Seepage is the only liquid discharge from sludge ponds and is dependent upon the type of liner used and whether the sludge is fixed or not	<2*	Evaporation of organics in sludge	Seepage	---	---V	---V

*Site specific

□Based upon 216,000 gal/day system capacity

ΔBased upon 30 inches/year effective net evaporation rate, and $1000/acre land cost

VCosts are not applicable on a flow rate basis

Two technologies, reverse osmosis and filtration, are included in Table 2-2 even though they appear to be applicable primarily as pretreatment steps. Any of the other technologies may use one or both of these processes for pretreatment prior to the main treatment process. Filtration may be required to remove solids and prevent plugging problems in such processes as activated carbon. Reverse osmosis may be used to reduce the quantity of effluent streams and thus reduce treatment costs for expensive processes such as vapor compression distillation.

The energy requirements for the selected control technologies presented in Table 2-2 vary greatly between the controls. For example, brine concentration is very energy intensive, and, therefore, is most cost-effective when treating streams that have been concentrated and/or pretreated.

The data gathered for many of the control technologies were not of sufficient quality to accurately assess cost versus wastewater flow rate or to determine the effectiveness of the control method for the various priority pollutants. For these controls, available data were presented and used for rough comparisons. However, additional information should be obtained on those processes that continue to appear applicable to utility effluents in subsequent studies to better define their performance characteristics.

The results of the study indicate that there are several control alternatives that can potentially control the priority pollutants present in utility effluents. However, a more complete definition of the pollutants in utility streams will be required to determine the most appropriate controls. Also, since the operational characteristics and water management strategies are different from plant to plant, different priority pollutant control strategies will be required depending on the situation.

CONCLUSIONS

This preliminary assessment of technology for the control of priority pollutants in electric utility industry wastewaters resulted in the following conclusions:

1) Wastewater control technologies have been identified that have a high potential for controlling the priority pollutants present in electric utility industry wastewaters.

2) Some of the control technologies reviewed in this report have been used for wastewater treatment in the electric utility industry. These include vapor compression distillation and evaporation ponds. Such technologies should be useful in removing certain priority pollutants from wastewaters. However, their effectiveness has not been confirmed in removing certain materials at present and secondary emissions associated with ultimate disposal could reduce their overall effectiveness.

3) The applicability of carbon adsorption has not been demonstrated in the utility industry. Chemical precipitation and reverse osmosis have been used in some applications but not for the control of a large number of the priority pollutants. These technologies have a high potential for effectiveness in removing priority pollutants.

4) A major problem in projecting control technology effectiveness data for the utility industry is the low priority pollutant concentrations expected. Once these technologies are evaluated in applications involving these low concentrations, it will be possible to make more definitive judgements about them.

RECOMMENDATIONS

This assessment of technology for the control of effluents from the electric utility industry resulted in the following recommendations:

1) The control technologies evaluated as having the highest potential for removal of priority pollutants should be further defined in the following areas:

   - control effectiveness and cost data for the processes should be gathered in an operating utility plant test program
   - secondary emissions and techniques for their control should be further defined.

2) Additional analytical work should be performed to identify specific compounds and complexes in utility streams to further assess both their toxicity and potential strategies for their control. This is especially applicable to heavy metals.

3) From subsequent studies, typical utility control situations should be determined and more reliable assessments of control alternative cost and effectiveness should be performed.

4) Since water treatment costs are a function of flow rate, it is anticipated that recycle/reuse strategies will be employed in utilities to reduce effluent rates. The impact of recycle/reuse alternatives on utility treatment options should be assessed.

SECTION 3

IDENTIFICATION OF POLLUTANT SOURCES IN EFFLUENT STREAMS FROM UTILITY POWER PLANTS

As discussed in the introduction, only preliminary data were available on the concentrations of priority pollutants in utility effluent streams. To properly assess the feasibility of applying wastewater treatment technologies to those streams, more specific information was needed to identify not only the existence of priority pollutants in the effluents but also the mechanisms by which these materials enter the various utility water systems.

The sources of priority pollutants present in utility wastewater were identified as a result of the following three step procedure:

- identification of wastewater streams in utility power plants,
- identification of chemical additives or other sources of chemicals that impact priority pollutants concentrations in the wastewater streams identified in the first step, and
- identification of significant priority pollutants which are added to the system.

Information was collected by the above procedure to characterize the utility plant streams as follows:

- identify general stream characteristics, such as pH and physical relationship to plant, and
- identify sources of chemicals and concentrations in the streams, especially for priority pollutants.

This type of information is necessary to provide a preliminary basis for the evaluation of the suitability of the control technologies for utility streams. The performance of the various control technologies may be very dependent upon the characteristics of the stream to which it is applied, such as pH, flow rate, priority pollutants concentration, etc.

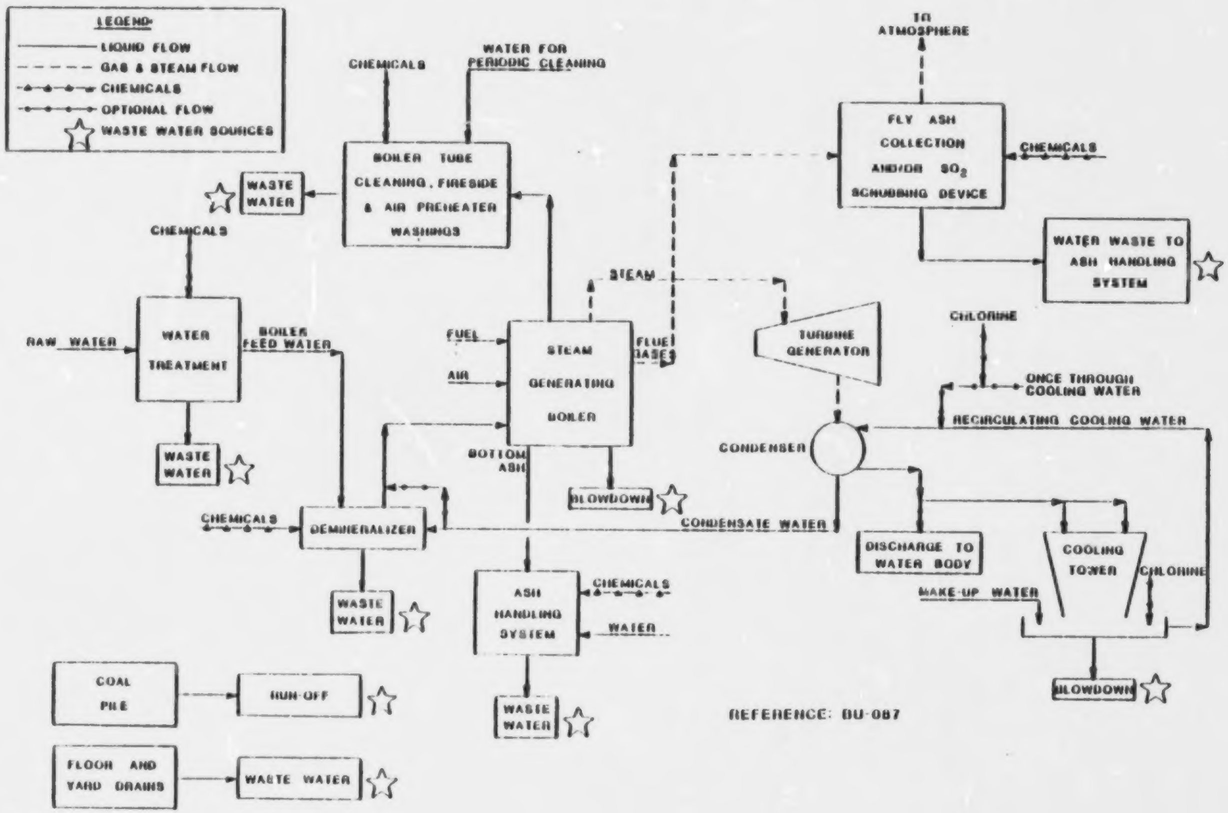
Water system arrangement alternatives or water management within a power plant is also dependent upon the characteristics of utility streams. Water management involves the use of water recycle/reuse strategies and can result in the reduction of plant effluent rates. While this report examines end-of-pipe treatment, water management schemes based on utility water stream characteristics can have a very significant impact on the quantity and quality of plant effluents, perhaps strongly affecting applicability and economics of the treatment process.

UTILITY EFFLUENT STREAMS

The steam-electric power industry uses large quantities of water, primarily for cooling purposes. There are, however, several other water utilizing processes which produce wastewater streams. The quality of wastewater from these processes varies considerably depending on intake water quality and/or the chemical character of the fuel used. Generalized descriptions of the water utilizing processes and the wastewater streams associated with them are contained in this section.

Figure 3-1 graphically summarizes the sources of wastewater in a fossil fuel generating station and depicts the interrelation of the various processes producing these waters. The sources of wastewater are:

- cooling water systems,
- boiler operations,
- ash handling,
- coal storage and handling,
- water treatment,
- general plant drainage,
- process spills and leaks, and
- miscellaneous operations.


LEGEND:
LIQUID FLOW
GAS & STEAM FLOW
CHEMICALS
OPTIONAL FLOW
WASTE WATER SOURCES
CHEMICALS
WATER FOR PERIODIC CLEANING
BOILER TUBE CLEANING, FIRESIDE & AIR PREHEATER WASHINGS
WASTE WATER
CHEMICALS
RAW WATER
WATER TREATMENT
BOILER FEED WATER
WASTE WATER
TO ATMOSPHERE
FLY ASH COLLECTION AND/OR SO2 SCRUBBING DEVICE
CHEMICALS
WATER WASTE TO ASH HANDLING SYSTEM
STEAM
FUEL
AIR
STEAM GENERATING BOILER
FLUE GASES
BOTTOM ASH
BLOWDOWN
TURBINE GENERATOR
CHLORINE
ONCE THROUGH COOLING WATER
RECIRCULATING COOLING WATER
CONDENSER
CONDENSATE WATER
CHEMICALS
DEMINERALIZER
WASTE WATER
ASH HANDLING SYSTEM
CHEMICALS
WATER
WASTE WATER
DISCHARGE TO WATER BODY
COOLING TOWER
CHLORINE
MAKE-UP WATER
BLOWDOWN
COAL PILE
RUN-OFF
FLOOR AND YARD DRAINS
WASTE WATER

REFERENCE: BU-087

Figure 3-1. Sources of wastewater in a fossil-fueled steam-electric plant.

The various water systems and wastewater sources were surveyed to characterize the water streams and identify their relationship with plant operations. The findings are summarized and presented in Appendix A.

PRIORITY POLLUTANTS IN EFFLUENT STREAMS

Priority pollutants potentially present in utility wastewater streams were identified in a previous EPA study (see Table 1-2). The 51 priority pollutants listed in that table were reduced to 31 by creating several general categories (i.e., chlorinated benzenes, chlorinated alkalenes, chlorinated phenols, etc.). The potential sources of these compounds or classes of compounds are identified in Table 3-1.

Radian's survey of the effluent streams and chemical compositions of these streams was used to generate the data in Table 3-2. Detailed information on the streams identified is presented in Appendix A.

Table 3-2 summarizes the chemicals added to streams or the compounds entering the various streams from such sources as ash dissolution or boiler tube cleaning. This links the priority pollutants potentially present in the various utility effluent streams to the treatment chemicals added to those streams. The chemicals listed as additives in the table are those common to water treatment for the indicated use.

TABLE 3-1. PRIORITY POLLUTANTS POTENTIALLY PRESENT IN UTILITY EFFLUENTS

Sources Toxic Species Potentially Present in Utility Effluents	Corrosion and scale inhibitor	Corrosion inhibitor	Cooling system treatment	Condensate neutralizer	Cleaning product	Ash constituent	Construction material	Cooling tower material	Insulation	Maintenance material	Transformer fluid	Lab reagent	Instrument use
Acrolein			x										
Antimony and compounds						x							
Arsenic and compounds			x			x							
Asbestos								x	x				
Benzene			x									x	
Beryllium and compounds						x	x						
Cadmium and compounds						x	x						
Carbon tetrachloride			x									x	
Chlorinated benzenes			x										
Chlorinated ethanes					x							x	
Chloroalkyl ethers			x										
Chlorinated phenols			x							x			
Chloroform												x	
Chromium and compounds	x					x	x						
Copper and compounds		x				x	x						
Cyanides	x		x			x							
2,4-Dichlorophenol			x		x								
Lead and compounds						x							
Mercury and compounds			x			x							x
Naphthalene												x	
Nickel and compounds						x	x						
Nitrosamines				x									
Pentachlorophenol			x		x								
Phenol										x			
Polychlorinated biphenyls											x		
Polynuclear aromatic hydrocarbons										x			
Selenium and compounds						x							
Silver and compounds						x							
Thallium and compounds						x							
Toluene					x							x	
Zinc and compounds			x			x	x						

Source: Preliminary EPA data

TABLE 3-2. SUMMARY OF CHEMICAL CHARACTERISTICS OF UTILITY EFFLUENT STREAMS

Effluent Stream	Process or Operation	Chemical Additive(s)	Typical Conc. of Additive or Pollutant	Resulting Priority Pollutant Expected in Effluent	Expected Conc. of Pollutants in Effluent	Comments
Cooling Tower Blowdown	Corrosion Inhibition	Chromate	10-50 mg/ℓ as CrO_4	Chromium	10-50 mg/ℓ	
		Zinc	8-35 mg/ℓ as Zn	Zinc	8-35 mg/ℓ	
		Phosphate	15-60 mg/ℓ as PO_4			
		Silicates	---			
		Proprietary Organics	3-10 mg/ℓ as organic	Potential priority organics		Organics can react with residual chlorine to form chlorinated compounds
	Scale Control	Acid (H_2SO_4)				
		Inorganic Polyphosphates	2-5 mg/ℓ			
		Chelating Agents	---			
		Polyelectrolyte Antiprecipitants	1-2 mg/ℓ			
		Organic/Polymer Dispersants	20-50 mg/ℓ	Potential priority organics		Organics can react with residual chlorine to form chlorinated compounds
	Biological Fouling (Algae, Slimes, Fungi) Control	Chlorine	<0.5 mg/ℓ residual Cl_2			Supplies free chlorine for reaction with organics to form chlorinated organics
		Hypochlorite	---			
		Chlorophenates		Chlorinated Phenols		
		Thiocyanates		Cyanide		
		Organic Sulfur Compounds	~30 mg/ℓ residual concentrations			
	Suspended Solids Dispersion	Tannins				
		Lignins				
		Proprietary Organics/Polymers	20-50 mg/ℓ	Potential priority organics		Organics can react with residual chlorine to form chlorinated compounds
		Polyelectrolytes/ Nonionic Polymers	1-2 mg/ℓ			
	Leaching of wood preservatives from wood cooling towers	Acid Copper Chromate	Unknown	Chromium		
		Chromated Copper Arsenate	Unknown	Arsenic		
		Creosote	Unknown			
		Pentachlorophenol	Unknown	Pentachlorophenol		

(Continued)

TABLE 3-2. (Continued)

Effluent Stream	Process or Operation	Chemical Additives(s)	Typical Conc. of Additive or Pollutant	Resulting Priority Pollutant Expected in Effluent	Expected Conc. of Pollutants in Effluent	Comments
Boiler Water Systems	Scale Control	Di & Tri Sodium Phosphates	3-60 mg/ℓ of PO_4			
		Ethylene diaminetetracetic acid (EDTA)	20-100 mg/ℓ			
		Nitrolatriacetic acid (NTA)	10-60 mg/ℓ			
		Alginates	50-100 mg/ℓ			
		Polyacrylates	50-100 mg/ℓ			
		Polymethacrylates	50-100 mg/ℓ			
	Corrosion Control	Sodium Sulfite	<200 mg/ℓ			
		Hydrazine	5-45 mg/ℓ			
		Morpholine	5-45 mg/ℓ			
	pH Control	Sodium Hydroxide Sodium Carbonate Ammonia Morpholine Hydrazine	variable added to adjust pH to 8-11.0			
	Solids Deposition	Starch	20-50 mg/ℓ			
		Alginates	20-50 mg/ℓ			
		Polyacrylamides	20-50 mg/ℓ			
		Polyacrylates	20-50 mg/ℓ			
		Tannins	<200 mg/ℓ			
		Lignin Derivatives	≤200 mg/ℓ			
		Polymethocrylates	20-50 mg/ℓ			
	Ion Exchange Water Treatment	Regenerant Solutions added to reactivate bed		Priority pollutants present in source water	Significantly higher concentrations than source water	
	Chemical Cleaning					
	• boiler waterside cleaning and condenser waterside cleaning	Acid Solvents and Toxic Solvents		Nickel Zinc Aluminum Copper		Heavy metals are dissolved into the cleaning solution from equipment surfaces
	• boiler fireside	Water or slightly alkaline wash Na_2CO_3 NaOH Phosphates		Iron nickel chromium vanadium zinc		Much of the priority pollutants come from dissolution of deposits on boiler tube surfaces. The deposits originate in the coal or oil burned.

(Continued)

TABLE 3-2. (Continued)

Effluent Stream	Process or Operation	Chemical Additives(s)	Typical Conc. of Additive or Pollutant	Resulting Priority Pollutant Expected in Effluent	Expected Conc. of Pollutants in Effluent	Comments
Ash Handling	Ash Sluicing Coal Ash (fly ash and bottom ash)	None	Pollutant in sluice water before sluicing	In addition to Source Water: Cadmium Chromium Copper Lead Magensium Nickel		Trace metals in the coal or oil are leached into the sluicing liquor
	Oil Ash Sluicing			Vanadium Nickel Chromium		
Coal Pile Runoff	Rainfall/runoff			Iron Cadmium Beryllium Nickel Chromium Vanadium Zinc Copper		Dissolution of trace metals into water
General Plant Drainage	Rainfall/runoff			Any of the above pollutants depending on maintenance procedures at plant		
Process Spills and Leaks	Accidents involving general plant operations			Any of the above pollutants depending on where the wastewater originates		
Miscellaneous Operations						

SECTION 4

PRELIMINARY SURVEY OF PRIORITY POLLUTANT CONTROL TECHNOLOGIES

A preliminary survey was conducted to identify technologies currently in use which have exhibited some control of priority pollutants in effluents from the electric utility industry. In addition to the utility industry, other industries were examined for control technologies potentially applicable. The non-utility industries surveyed were:

- Petroleum Refining,
- Chemical Producing,
- Metal Plating,
- Metal Finishing,
- Mining and Ore Dressing, and
- Metal Smelting.

As discussed in Section 3, effluent producing processes at power plants for which control technologies were examined include:

- Cooling Water Systems,
- Boiler Operations,
- Ash Handling,
- Coal Pile Runoff,
- General Plant Drainage,
- Process Spills and Leaks, and
- Miscellaneous Sources.

End-of-pipe treatment technologies were identified which have exhibited some control effectiveness for the priority pollutants identified in utility streams. Information on the performance of the controls was obtained for the most part from applications to waste streams from non-utility industries. Therefore, the performance is not always related to the priority pollutant concentration or other stream characteristics that would normally be encountered in utility streams.

A preliminary assessment was then made for each control technology identified to evaluate its potential for use by utilities. Those judged most generally applicable were then subjected to a more detailed assessment.

STRATEGY

This survey was conducted using a number of readily available information sources. The major ones included:

- EPA Effluent Guideline Documents,
- EPA Water Pollution Control Research Series,
- Technical Journals and Publications, and
- Radian In-House Files.

In addition, vendors of control processes and equipment, and in some cases, industrial users were contacted to obtain current information on performance, applications, and costs. A process description summary sheet containing the following information was then prepared for each technology.

- Process Name,
- State of Development,
- Applications to Date,
- Process Description,
- Expected Performance,
- Costs,
- Secondary Process Emissions, and
- References.

The individual summary sheets for the technologies identified in the preliminary survey are presented in Appendix B.

The findings of the preliminary survey were screened to select technologies for the control of priority effluents which justified further in-depth evaluation. This screening process was based on the following criteria:

- Priority Pollutants Controlled,
- Effectiveness of Control,
- Applicability to Utility Streams,
- Process Reliability, and
- Commercial Availability.

A control technology was eliminated from further consideration when it clearly failed to meet one or more of the above criteria. The criteria that the eliminated control technologies failed to meet are presented in Appendix B.

The various control alternatives identified in the preliminary survey are summarized in Table 4-1. This summary table provides a basis for comparing the various control technologies so that the more applicable controls can be selected for further study.

SUMMARY OF PRELIMINARY SURVEY

The control technologies identified in the preliminary survey of the utility and non-utility industries are listed below.

Activated Carbon Adsorption
Activated Sludge
Aerated Lagoons
Air Oxidation
Alum Precipitation and Activated Carbon Adsorption
Barium Salt Precipitation
Chemical Oxidation
Chemical Reduction
Complex Formation and Activated Carbon Adsorption
Coprecipitation
Deep Well Disposal
Electrodialysis
Foam Fractionation
High Density Sludge Neutralization
Ion Exchange
Lime Neutralization and Precipitation
Liquid Waste Incineration
Photochemical Oxidation
Reverse Osmosis
Skimming and Flotation
Solvent Extraction
Sulfide Precipitation
Ultrafiltration

TABLE 4-1. PRELIMINARY SURVEY SUMMARY OF EFFLUENT CONTROL FOR THE ELECTRIC UTILITY INDUSTRY

Control Technology	Compounds Controlled	Effectiveness	Industry and Streams Applied to	Streams Applicable In Electric Utility	Economics	References
Activated Carbon Adsorption	Organics, suspended solids, ammonia	91-98% for BOD 60-90% for suspended solids 90-99% for phenols 33-87% for NH_3 70-95% for oil	Petroleum Refining	Coal Pile Runoff Yard Drainage Cooling Tower Blowdown Lab Drains Ash Pond Effluent	$0.67-$1.57 per gpd capital cost. $0.24-$0.55 per gpd annual cost. Also see preliminary survey process description.	EN-407 MI-265 BE-188 BU-215 VA-127 GI-121 ES-020 DA-052
Activated Sludge	Organics, suspended solids, ammonia, sulfides	80-99% for BOD 60-85% for suspended solids 95-99% for phenols 33-99% for NH_3 97-100$ for sulfides	Petroleum Refining Municipal wastewater Petrochemical	Coal Pile Runoff Yard Drainage Sanitary Wastes	$0.65-$1.00 per gpd for capital cost. $0.28-$0.40 per gpd for annual cost.	EN-407 BU-215 TE-111 BE-156
Aerated Lagoons	Organics, suspended solids, sulfides	75-95% for BOD 40-65% for suspended solids 90-99% for phenols 95-100% for sulfides 70-90% for oils 60-85% for COD	Petroleum Refining API Separator Effluent	Coal Pile Runoff Yard Drainage Sanitary Wastes	$0.20 per gpd for capital costs, very low annual cost due to minimum equipment.	EN-407 BU-215 KI-072 BE-156
Air Oxidation	Phenol	80-85% removal possible	Various industrial applications	Yard Drainage Coal Pile Runoff	$0.01/lb of phenol	EI-026
Algacide Substitution	Acrolein, arsenic, benzene, carbon tetrachloride, chlorinated benzene, chlorinated phenols, cyanide, mercury, nickel, pentachlorophenol, phenol, zinc	Total elimination of toxic algacides	Utility cooling water	Cooling tower Blowdown	~$5,000 capital investment. No change in operating costs.	EN-127 BR-394
Alum Precipitation and Activated Carbon Adsorption	Heavy metals and some organics	Metal % Removal Zn 28 Cr 97 Cu 98 Sb 71 Be 99 Cd 56 Pb 97 Se 56 Ag 99 Th 39 Hg 98 Ni 37	Municipal raw wastewater spiked with salts of heavy metals.	Cooling Tower Blowdown Ash Pond Effluent and Overflow Yard Drainage	See Preliminary Survey Process Description	CO-576 DA-052

TABLE 4-1. (Continued)

Control Technology	Compounds Controlled	Effectiveness	Industry and Streams Applied to	Streams Applicable In Electric Utility	Economics	References
Barium Salt Precipitation	Hexavalent chromium	1 ppm Cr^{+6} residual	Electroplating wastewater	Cooling Tower Blowdown Ash Pond Effluent and Overflow Boiler Blowdown Cleaning Wastes Water Pretreatment Wastes	No data available	SM-159
Chemical Oxidation	Cyanide and phenols	<0.001 ppm residual level for phenols and cyanides	Wastewater from mining, milling, and electroplating	Cooling Tower Blowdown Ash Pond Effluent and Overflow Boiler Blowdown Cleaning Wastes Water Pretreatment Wastes	Direct chemical costs for alkaline chlorination are $1.93/lb. CN^- oxidized.	RE-165 WI-260 EN-394 HO-293
Chemical Reduction	Cr^{+6} reduced followed by neutralization to precipitate Cr^{+3} and other heavy metals.	Typical results are 0.02 ppm Cr^{+6} and 0.01 ppm Cr^{+3} residual.	Metal finishing and electroplating waste water.	Cooling Tower Blowdown Ash Pond Effluent and Overflow Boiler Blowdown Cleaning Wastes Water Treatment Wastes	$0.50 per lb of $\dot{C}r$ treated using 11.5¢ per lb bisulfite and 6.5¢ per lb caustic	WI-260 SM-159 EN-127 EN-394
Complex Formation and Activated Carbon Adsorption	Cyanide and heavy metals	<1 ppm CN and Fe residual attainable	Electroplating waste water	Cooling Tower Blowdown Ash Pond Effluent and Overflow Boiler Blowdown Cleaning Wastes Water Pretreatment Wastes	$0.16-$0.87 per lb CN operating cost	RE-165
Coprecipitation	Ra, Mo	1 picogram/ℓ Ra residual 0.02-0.1 ppm Mo residual	Control of radium in uranium industry, control of molybdenum in feroalloy industry.	Cooling Tower Blowdown Ash Pond Effluent and Overflow Boiler Blowdown	No data available	EN-394
Deep Well Disposal	Phosphate, Fe, Cu, Al, An	100%	Oil field brine and chemical wastes.	All	Extremely site-specific.	EN-392 EN-127
Electrodialysis	Desalination ionic dissolved solids	60-98% removal of dissolved solids	Desalination	Cooling Tower Blowdown Yard Drainage Boiler Blowdown Coal Pile Runoff	$0.40-$0.50 per 1000 gal operating cost	EN-394 KI-160 Vendor Contacts
Electrolytic Oxidation	Phenol	95%	Experimental	Yard Drainage Coal Pile Runoff	$1.53-$3.06/lb of phenol	EI-026
Electrolytic Reduction	Chromium	0.05 ppm residual	Refining, Petrochemical, Cooling Tower Blowdown	Cooling Tower Blowdown	$500,000 capital $138,000 operating costs for 500 gpm	DI-150 DU-134
Evaporation	All	100%	Mining and milling operations and some utilities in western and southwestern states.	All	Site-specific	EN-394 EN-392

TABLE 4-1. (Continued)

Control Technology	Compounds Controlled	Effectiveness	Industry and Streams Applied to	Streams Applicable in Electric Utility	Economics	References
Ferric Chloride Precipitation and Activated Carbon Adsorption	Heavy metals	Metal % Removal Zn 94 Cr 99 Cu 96 Sb 72 Be 99 Cd 99 Pb 98 Se 80 Ag 99 Th 45 As 97	Municipal raw wastewater spiked with salts of heavy metals.	Cooling Tower Blowdown Ash Pond Effluent and Overflow Yard Drainage	See Preliminary Survey Process Description	CO-576 DA-052
Foam Fractionation	Phenol	85%	Developmental Stage	Yard Drainage Coal Pile Runoff	$0.09 per cb phenol	EI-026
High Density Sludge Acid Neutralization	Acid and heavy metals	Heavy metals removal pH dependent	Acid or mine wastewater	Cooling Tower Blowdown Ash Pond Effluent and Overflow Yard Drainage	No data available	EN-394
Ion Exchange	Trace metal, cyanide, phenols	Trace metals 0.001-0.4 ppm residual <0.1 CN	Widespread commercial use, demineralize boiler feed water, etc.	All except sanitary and pretreatment waste	$275,000 capital cost for 500,000 gpd system, $1.79 O&M per 1000 gal treated	MA-693 DI-150
Lime Neutralization	As, Cd, Cu, Cr^{+3}, Fe, Hg, Mn, Ni, Pb, An and heavy metals generally.	Example of residual levels that are attainable. As 0.05 ppm Cd 0.05 Cu 0.03 Cr^{+3} 0.05 Fe 1.0 Hg 0.0001 Mn 1.0 Ni 0.05 Pb 0.10 Zn 0.15	Widespread commercial use	Cooling Tower Blowdown Ash Pond Effluent and Overflow Boiler Blowdown Cleaning Wastes Water Treatment Wastes Yard Drainage	$150,000 capital and $53,000/year operating cost in 1971 dollars for 100 gpm wastewater	EN-391 EN-392 EN-393 EN-394
Lime Precipitation and Activated Carbon Adsorption	Heavy metal and some organics	Metal % Removal Hg 91 Ni 99 Zn 76 As 84 Cu 90 Sb 52 Be 99 Cd 99 Pb 99 Se 95 Ag 98 Th 72	Municipal raw wastewater spiked with salts of heavy metals.	Cooling Tower Blowdown Ash Pond Effluent and Overflow	See Preliminary Survey Process Description.	CO-576 LA-261 DA-052

TABLE 4-1. (Continued)

Control Technology	Compounds Controlled	Effectiveness	Industry and Streams Applied to	Streams Applicable In Electric Utility	Economics	Reference
Liquid Waste Incineration	Organic cleaning compounds such as chlorinated phenols, ethane, and toluene	100% effective for liquid effluents	Petrochemical, refining, and chemical industry cleaning wastes.	Boiler waterside cleaning wastes	No pertinent data available	UT-029 AZ-009 LU-013
Photochemical Oxidation	Phenol	70% removal possible	Laboratory Investigation	Yard Drainage Coal Pile Runoff	$0.22-$0.26 per cb phenol	EI-026
Reverse Osmosis	Desalination Heavy metals Organics	+90% removal of dissolved solids +95% removal of organics	Desalination, acid mine water, metal finishing wastewater	All	Approximately $1.00/gpd capital cost $0.75 per gal operating and maintenance	EN-394 DI-149
Skimming and Flotation	Oil	Variable	Petrochemical, refining, mining wastewater	Yard drainage	No data available	EN-392
Solvent Extraction	Phenols	No data available	Refining, mineral processing	Yard Drainage Coal Pile Runoff Cleaning Wastes	No data available	MA-246
Sulfide Precipitation	Ni, Cd, Pb, Zn, Hg	Less than 1 ppm residual; avg 97% removal of Hg	Commercially available but little used due to toxicity of H_2S and metal sulfides. Some application for mining and milling wastewaters.	Cooling Tower Blowdown Ash Pond Effluent and Overflow Boiler Blowdown Cleaning Wastes Water Treatment Wastes	For mercury cell chlor-alkali plant capital cost $143,000 Operating cost 50¢/1000 gal.	EN-391 EN-394
Ultrafiltration	Oil and high molecular weight compounds	Retain material of molecular weight of 500 or more	Petrochemical, refining, mining wastewater	Yard Drainage	No data available	EN-394
Ultrasonic Oxidation	Phenol	100%	Experimental	Yard Drainage Coal Pile Runoff	No data available	EI-026
Vapor Compression Distillation	All	100%	Utility	All	Capital costs: $1-2 million per 100 Mgpd cap. O&M Costs: $1.80-2.00 per 1000 gals treated	LE-299 BO-290
Zero Discharge Strategies	All	100%	Utility	All	Site-specific	EN-127

Electrolytic Oxidation
Electrolytic Reduction
Evaporation
Ferric Chloride Precipitation
  and Activated Carbon Adsorption
Ultrasonic Oxidation
Vapor Compression
  Distillation
Zero Discharge Strategies

Description sheets for these processes can be found in Appendix B. Information summarizing the pertinent features of the processes is given in Table 4-1.

EVALUATION OF RESULTS

The wastewater control techniques just listed were evaluated using the criteria outlined at the first of this section. The objective was to identify those processes with the most potential for removing priority pollutants in utility plant effluent streams. Those processes were then examined in more detail. As a result of this evaluation, the processes listed below were selected for further analysis:

- Activated Carbon,
- Precipitation,
- Evaporation Ponds, and
- Vapor Compression Distillation.

In addition, reverse osmosis and filtration were evaluated as pretreatment processes. Solid waste disposal techniques were also evaluated as a means of controlling secondary solid wastes resulting from wastewater controls.

SECTION 5

ASSESSMENT OF SELECTED CONTROL TECHNOLOGIES

This section presents the methodology and results of the preliminary evaluation of the effluent control technologies deemed most applicable to utilities. A description of the assessment techniques used to evaluate the selected processes, and a discussion of each technology evaluated is presented. The process evaluation subsections include a brief process description and flow sheet, the effectiveness of control for the appropriate species, and capital and operating costs. The process summaries also address the state of development and applications to date, energy requirements, and secondary process emissions. The applicability of each technology to steam/electric utility streams is discussed.

METHODOLOGY FOR THE TECHNICAL AND ECONOMIC ASSESSMENT OF THE SELECTED PROCESSES

The methodology used for completing the preliminary assessment of the selected technologies to control effluents from the utility industry is discussed below. The results of the assessment are presented in the remainder of Section 5.

The assessment of the selected control processes consists of two parts:

- technical
- economic

Both types of assessments of the selected controls were conducted by extending the broad literature survey of processes begun in Section 4 to focus on the specific processes. The additional information from the process specific literature survey was combined with that from the preliminary survey to provide the data base for the assessment of the selected processes. When appropriate, vendors of wastewater treatment systems were contacted to gather technical and economic information on the selected processes to augment the information obtained from the literature survey.

Technical Assessment

The major thrust of the technical assessment was to evaluate the applicability of the selected control technologies to the utility industry. For the controls not presently used in the utility industry, this involved an engineering assessment of the ability of the control technologies to remove the materials for which they were identified to be effective. This evaluation required that the mechanism for pollutant removal by each process be compared on a chemical and engineering basis to the chemical and physical characteristics of the utility streams as presented in Section 3.

In general, at the time of this study, the priority pollutants which are present in utility streams and their concentrations are poorly defined. Also, the available information on the effectiveness of control technologies for reducing priority pollutants is related primarily to industries other than the utility industry. As a result, the estimates of the performance and costs for the control of the priority pollutants are not based upon specific utility data. However, efforts were made to interpret the available information and apply it to the utility situation.

As part of the technical evaluation, the following specific items were examined:

- state of development - the degree to which the technologies have been developed and applied from bench-scale to commercial scale application,
- applications to date - the industry and, where possible, specific application of the control technology,
- process description - the general description of the process and the mechanism for priority pollutant reduction,
- expected performance - the comparison of the performance of the control technology in the industry it is used to the expected performance in the utility situation,
- energy requirements - the energy directly associated with the control technology in the utility situation, and

- secondary process emissions - the air, water, and solid emissions of priority pollutants resulting from the application to wastewater streams of the control technology, e.g., vents, blowdown streams, sludges, backwash water, and process wastes.

Economic Assessment

The data base for the economic assessment of the selected technologies was established in the same manner as that for the technical assessment. After the process specific literature survey was completed and appropriate vendors were contacted, the economic information was examined for consistency between sources and applications. The control technology costs which were determined to be most applicable to the utility situation were selected for further assessment.

The capital and operating costs for each process were determined as a function of stream flow rate and characteristics. When appropriate for the various controls, the site specific impacts of the controls upon costs were identified. However, the cost of site specific aspects were not assessed. All costs were adjusted to 1977 dollars using standard engineering cost escalation indices.

The capital costs are total installed capital costs and include equipment, engineering, and overhead. Costs for retrofitting are not included due to the highly site-specific nature of applying the controls to the utility industry and the lack of a firm data base relating to the utility situation. Operating costs include raw materials, labor, energy requirements, and maintenance. The energy requirements are confined to those directly associated with the control technology.

ACTIVATED CARBON ADSORPTION

Activated carbon adsorption has been widely applied in the field of water and wastewater treatment. With the development of high surface area carbon that could be reactivated, carbon adsorption has emerged as an economically practical and efficient wastewater treatment system for organic pollutant removal in many industries.

The overall flexibility of the carbon adsorption process has resulted in its application in a wide variety of situations. Carbon adsorption is currently being used in the following industries:

- Detergent manufacturing where xylene, alcohols, and TOC are removed from effluent wastewater,
- Oil refining where COD is removed from effluent wastewater,
- Chemicals manufacturing where phenols and resin intermediates are removed from wastewater,
- Resin manufacturing where xylene and phenols are removed from effluent wastewater,
- Herbicide manufacturing where toxic phenols are removed from wastewater,
- Coking plants where phenols are removed from ammonical liquor, and
- Municipal wastewater plants.

Process Description

Carbon adsorption systems designed for utility wastewater treatment would consist of carbon bed contact equipment, pretreatment facilities, if necessary, and carbon regeneration facilities, if economically practical. Pretreatment equipment is needed if excessive quantities of suspended solids, oils, or grease are present. If not removed, these constituents would otherwise filter out on the carbon beds and increase the pressure drop. Pretreatments commonly used are chemical clarification, oil flotation, and filtration. Following pretreatment, the wastewater is contacted with the activated carbon beds. The beds may be arranged in several different configurations. Some common ones include:

- fixed beds in series,
- moving beds,
- fixed beds in parallel, and
- upflow expanded beds.

An important consideration in the design and proper operation of a carbon adsorption system is the contact time or residence time of the water in the carbon bed. The optimum contact time for a given carbon system is dependent upon several conditions, including the type and concentration of organics being removed, stream pH, stream temperature, and effluent quality. Since the organic concentrations and especially the priority organic concentration of utility plant effluents are generally low, special consideration should be given to these conditions as to how they affect the carbon selectivity and, ultimately, bed contact time. The relationship between contact time and residual concentration of organics would need to be determined for each adsorption system installed.

Several general rules can be applied to predict preferential adsorption of organics by carbon. High-molecular-weight organic molecules of a given class adsorb preferentially to those in the same class having lower molecular weights. Also, nonpolar organic molecules are preferentially adsorbed over polar organics. Very little information, however, is available on the effectiveness of carbon treatment on industrial wastewaters with very low concentrations of organics as found in most utility applications.

Other major factors affecting adsorption specificity is stream pH and temperature. The pH affects the solubilities of various organics and, therefore, their capacity for adsorption. The temperature of the stream being treated can affect activated carbon's performance as well. Higher temperatures can increase the solubility of certain organic compounds, therefore hindering their adsorption on activated carbon.

Once the carbon bed becomes saturated, or breakthrough occurs, the bed must be taken offstream. Treatment of the saturated carbon is based on economic considerations. Options available include disposal of the used carbon or either on-site or off-site regeneration. Basically, for systems which need to regenerate less than about two hundred pounds per day of carbon, it is more economical to dispose of the carbon or use off-site regeneration. For large carbon regeneration requirements, on-site equipment is economically attractive. Regeneration is accomplished by thermally partially oxidizing used carbon in either multiple-hearth furnaces or rotary kilns to reactive exhausted carbon for reuse. Heating exhausted carbon to 1500-1800°F drives off moisture and volatilizes the organic contaminants. The off gas from the regeneration step is routed to an incinerator to reduce secondary emissions. Due to attrition, about 5-10 percent of the carbon sent to regeneration is lost. Figure 5-1 illustrates a carbon adsorption/regeneration system.

Control Effectiveness

Carbon adsorption is capable of removing certain organic species found in utility wastewater streams. Table 5-1 presents some reported control efficiencies for carbon adsorption. The data reported in the table for acrolein, benzene, and toluene

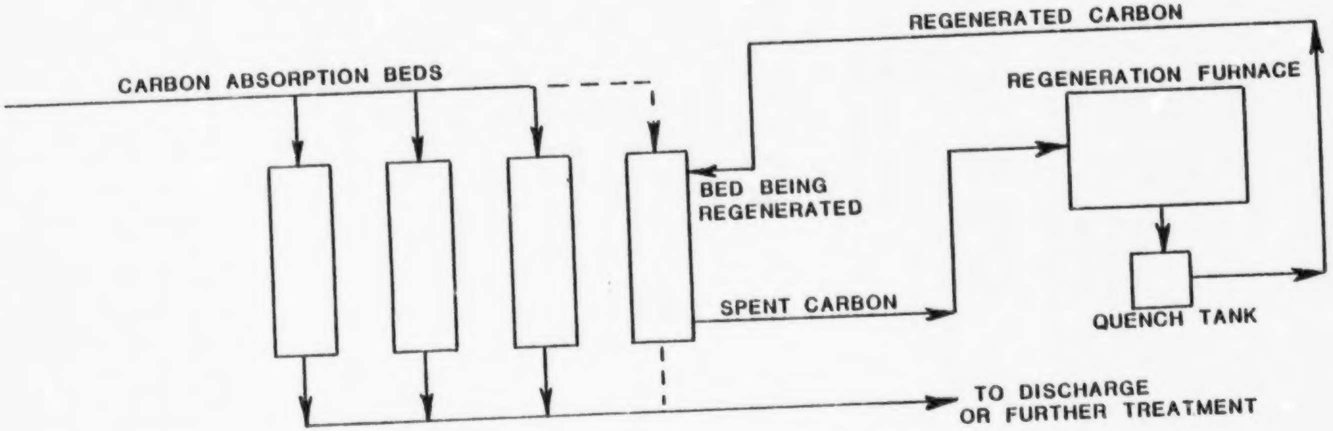

REGENERATED CARBON
CARBON ABSORPTION BEDS
REGENERATION FURNACE
BED BEING REGENERATED
SPENT CARBON
QUENCH TANK
TO DISCHARGE OR FURTHER TREATMENT

Figure 5-1. Downflow in parallel carbon adsorption/regeneration system.

TABLE 5-1. CARBON ADSORPTION TOXIC POLLUTANT REMOVAL EFFECTIVENESS

Toxic Pollutant	% Removal Efficiency	Residual Concentration (mg/ℓ)
Acrolein	31	ND
Cyanides	1	ND
Phenol	99	0.005
Benzene	95	ND
Toluene	79	ND

ND - no data

References: GI-121, VA-127, PA-120.

are based upon bench-scale studies. As such, the numbers could differ significantly from what may be observed in a utility application. The cyanide and phenol data are based upon coke plant and refinery wastewater treatment data, respectively. Therefore, these numbers may be more representative, especially the phenol data, since the carbon system operated on low-organic concentration water such as might be found at utility plants.

Certain trace metals in municipal wastewaters have been removed to varying extents by carbon adsorption. Since activated carbon does not effectively remove dissolved metals through adsorption, it is suspected that the metal removal occurs through some other mechanism. One possible mechanism is the adsorption by the carbon of an organic molecule which has formed a complex with a metal. Whether or not metals removal through organic complexing would occur in utility wastewaters treated by carbon adsorption is unknown. For this reason no removal efficiencies for metals are reported for carbon adsorption.

Because carbon adsorption is effective for phenol, benzene, and toluene removal and to a limited extent acrolein, it is expected that this treatment process could be applied to the following streams:

- Coal Pile Runoff
- Yard Drainage
- Cooling Tower Blowdown
- Lab Drains
- Ash Pond Effluent

Costs

The costs associated with wastewater treatment by carbon adsorption are discussed below. Figures 5-2 and 5-3 present cost curves for carbon adsorption capital costs and operating and maintenance costs. The cost curves include on-site regeneration equipment above a flow of 800,000 gallons per day. This flow approximately represents the break-even-point above which on-site regeneration of the carbon becomes economical.

Capital costs for carbon adsorption are not only a function of the wastewater flow rate, but also of the carbon regeneration rate. The effect of different regeneration rates are shown in Figure 5-2. Curve I represents the capital cost for a system where the regeneration rate is 400 pounds of carbon per million gallons treated, Curve II is for a regeneration rate of 300 pounds per million gallons treated, and Curve III is for a regeneration rate of 200 pounds per million gallons treated.

Operating and maintenance costs are also a function of flow rate as well as the carbon regeneration rate. Regeneration rate is dependent upon the saturation of the bed and breakthrough of the least selectively adsorbed organic. The selectivity of adsorption on carbon of a given organic is a function of certain stream conditions as well as the nature of the organic compound, as discussed earlier. Figure 5-3 presents curves which show the effect of different regeneration rates. Curve I is for a regeneration rate of 400 pounds of carbon per million gallons treated and Curve III is for a regeneration rate of 200 pounds per million gallons treated.

Energy Requirements

Energy requirements for the adsorption step include pumping to overcome the pressure loss through the carbon beds. The estimated power requirements for pumping is 0.32 kW-hr/1000 gallons. This number is only approximate since the actual amount will vary with each system design and total dynamic head requirements (EN-088). For the systems using on-site regeneration, the energy requirements include the fuel needed for heating the spent carbon, generating steam for reactivation and for electricity to transport the carbon between adsorption and regeneration steps. The fuel required is estimated to be about 425,000 Btu per 100 pounds of carbon regenerated. The electrical power required is estimated to be 5.8 kW-hr per 100 pounds of carbon regenerated (EN-088). Off-site regeneration costs would include the 425,000 Btu per 100 pounds of carbon regenerated plus that for transportation.

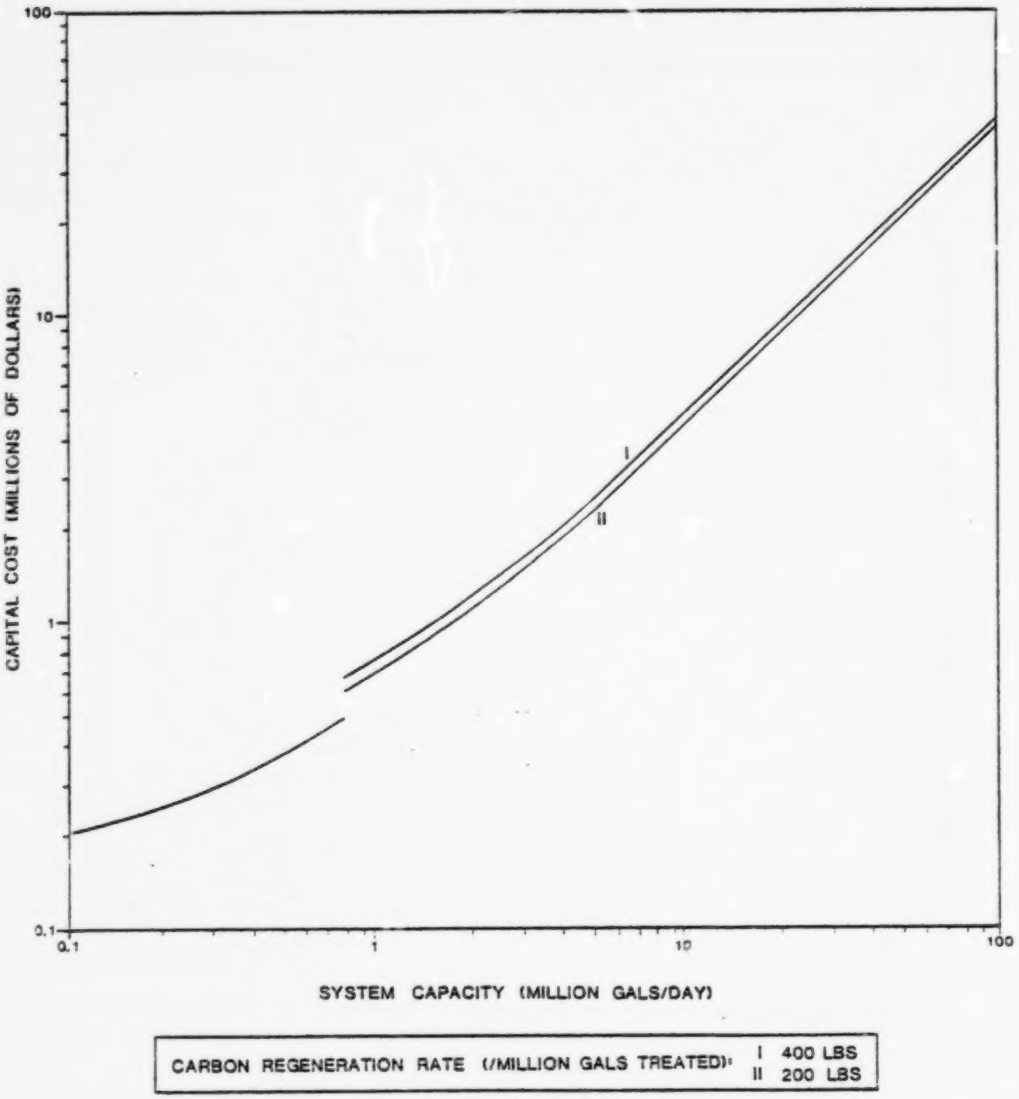


Figure 5-2. Carbon adsorption installed capital costs.

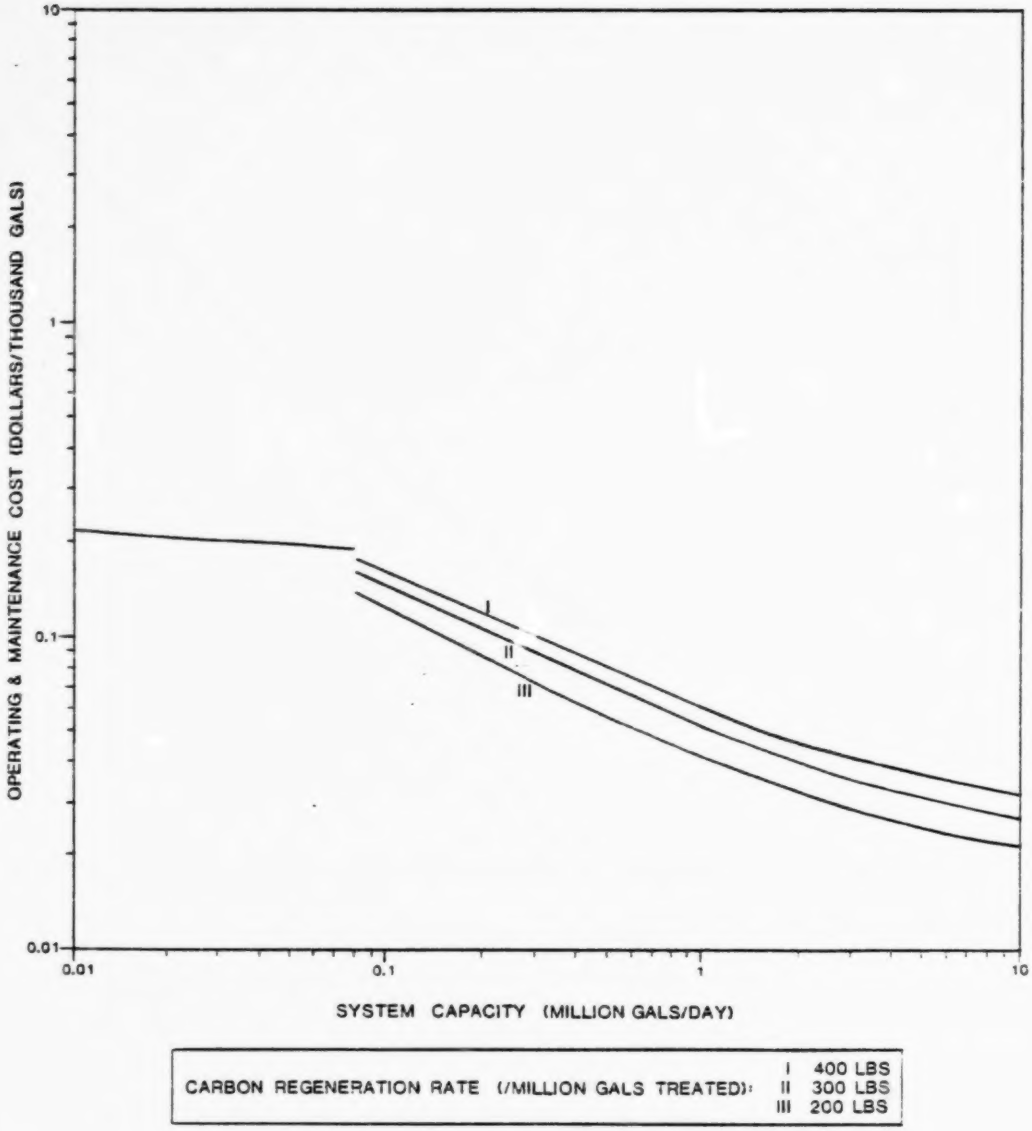


Figure 5-3. Carbon adsorption operating and maintenance costs.

Secondary Process Emissions

Secondary process emissions from carbon adsorption systems are associated entirely with the regeneration step. The hot regenerated carbon is cooled in a water quench step before being transported back to the beds. The quench water contains suspended solids which may need removing. Also, the stack gas from the carbon furnace may contain unoxidized organics and carbon fines. Incineration and scrubbing of the gas may be required if these pollutants are present in large quantities. Incineration and scrubbing were included in the costs for regeneration.

If the quantity of carbon is too small to justify regeneration, it can be disposed of in landfills. For coal-fired utilities, the carbon could be blended with the coal and combusted in the boiler. Organics adsorbed on the carbon are assumed to be completely oxidized in the boiler.

LIME PRECIPITATION

Lime precipitation is an effective and economical treatment process for removing dissolved metals from wastewaters. Lime precipitation has found extensive application in treating wastewaters from different industries. The following is a list of the industries which use lime precipitation:

- Electric utility industry
- Ore mining and dressing industry
- Metals plating industry
- Wood preserving industry
- Municipal water and wastewater treatment

Process Description

Lime precipitation removes contaminants by reducing their solubility and precipitating them from solution or by their coprecipitation with other insoluble compounds. Therefore, to be successful, lime precipitation depends primarily upon two factors:

- sufficient lime to drive the precipitation reaction to completion, and
- removal of the resulting solids from the treated stream.

A typical lime precipitation system is illustrated in Figure 5-4. Generally, the wastewater containing the contaminants to be removed is mixed in a tank with a slurry of lime and water to adjust the wastewater pH. The amount of lime added depends upon several parameters including stream alkalinity, pH, and metals concentration. The treated water is then discharged to a flocculation/clarification unit. This unit may be circular or rectangular. Rectangular units are usually more economical for larger flow rate applications.

In the flocculation/clarfication unit, coagulant aids and more lime may be added depending upon design consideration and wastewater characteristics. Formation of the insoluble compounds called floc is prompted by agitation and circulation of the water. Sedimentation of the floc is accomplished in a quiescent zone of the unit. Accumulated sludge is removed and may be processed in a thickener and vacuum filter or filter press for dewatering prior to disposal.

The treatment conditions, lime and coagulant dosages, and final pH must be optimized for any given waste stream, but, in general, a pH of at least 9 and as high as 12 may be necessary to insure removal of heavy metals. Figure 5-5 shows the relationship between pH and solubility for selected metals. However, the levels of concentration attainable in an actual operating system may vary from the limits predicted on the basis of the solubility curves in Figure 5.5 due to interfering species in the wastewater. Many factors, such as the effect of widely differing solubility products, mixed metal hydroxide complexing, and metal chelation may make theoretical limits presented in Figure 5-5 difficult or impossible to reach.

Control Effectiveness

Lime precipitation is capable of removing certain metals found in utility wastewaters. Among the metals removed by lime precipitation are: arsenic, cadmium, copper, trivalent chromium, manganese, nickel, lead, and zinc. Table 5-2 presents residual concentrations to which lime precipitation theoretically would be able to remove the above listed metals. This information is based upon published sources, industry data, and analysis of samples for the ferroalloy-ore mining and milling industry (EN-394). As mentioned, the data in Table 5-2 is not based upon utility plant applications. For this reason, it may not represent the results that might be expected from the application of lime precipitation to utility wastewaters. Factors which might alter the results for utilities are the much lower metals concentrations, organic-metal complexing, and differences in stream characteristics. In addition, other phenomena such as coprecipitation and floc entrapment can increase metals removal beyond solubility limitations.

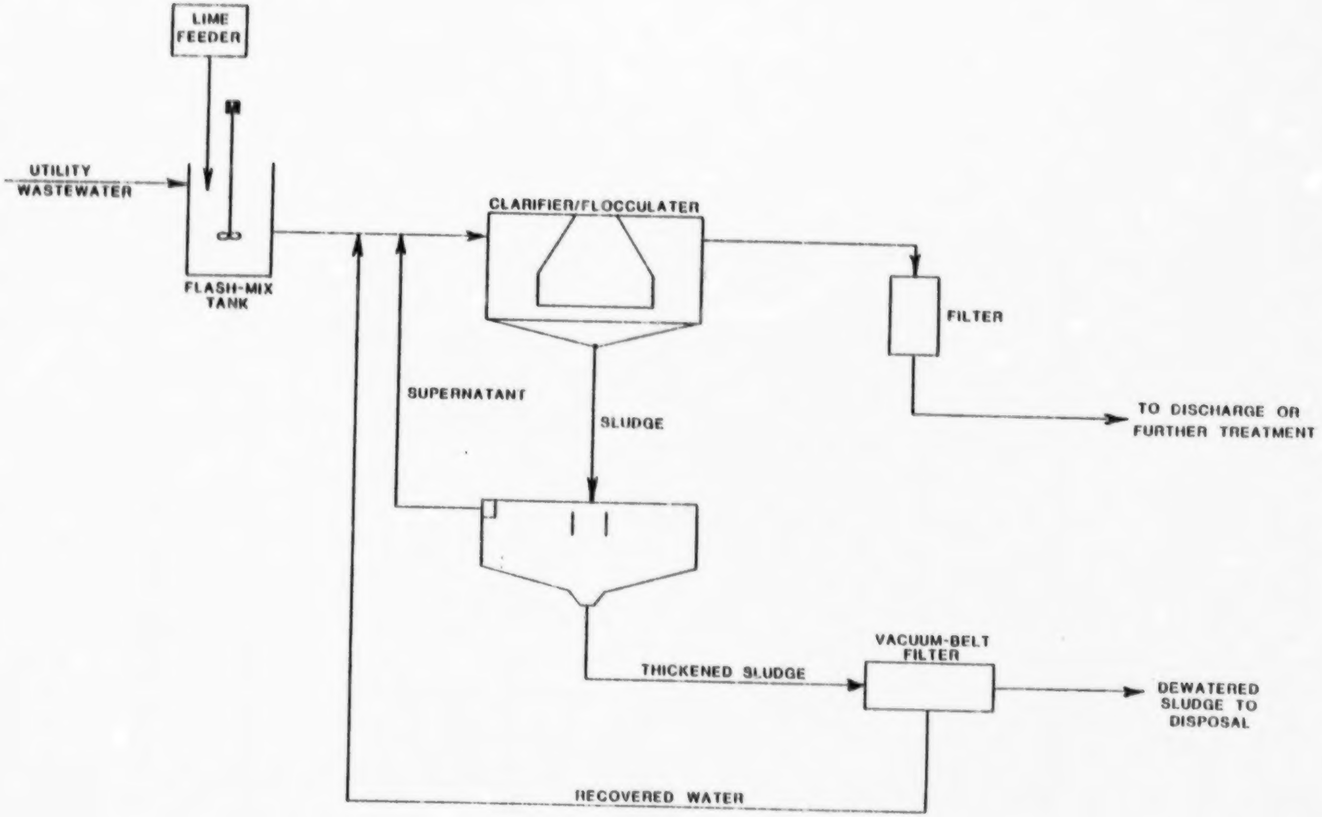
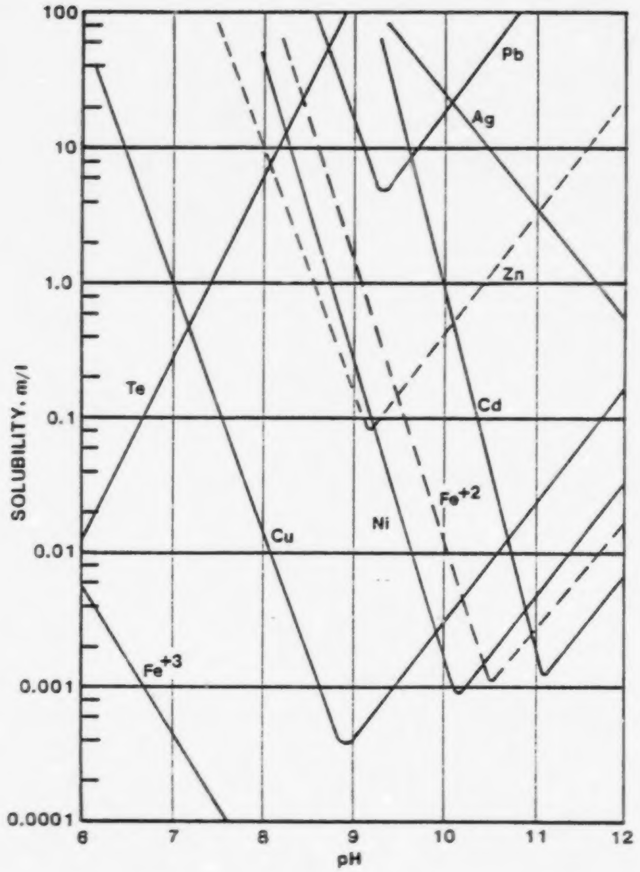

LIME FEEDER
UTILITY WASTEWATER
FLASH-MIX TANK
CLARIFIER/FLOCCULATER
FILTER
TO DISCHARGE OR FURTHER TREATMENT
SUPERNATANT
SLUDGE
THICKENED SLUDGE
VACUUM-BELT FILTER
DEWATERED SLUDGE TO DISPOSAL
RECOVERED WATER

Figure 5-4. Lime precipitation flow diagram.



SOURCE: ADAPTED FROM REFERENCE EN-127

02-1489-1

Figure 5-5. Theoretical solubilities of metal ions as a function of pH.

TABLE 5-2. LIME PRECIPITATION POLLUTANT REMOVAL EFFECTIVENESS

Toxic Pollutant	Residual Concentration (mg/ℓ)
Arsenic	0.05
Cadmium	0.05
Copper	0.03
Trivalent chromium	0.05
Manganese	1.0
Nickel	0.05
Lead	0.10
Zinc	0.15

Source: EN-394, PA-120

More work is needed in determining the effectiveness of lime precipitation for removing metals from utility effluents. Several aspects should be given special consideration. Coprecipitation is a mechanism which is not discussed in the literature that may enable metals in utility effluents to be removed below their theoretical solubilities. It is also suspected that the flocculation step in precipitation systems could remove by physical enmeshment some organics from utility wastewater streams. More information is needed on the potential removal mechanism.

Based on typical utility wastewater characteristics and the ability of lime precipitation to control the listed metals, this control process may potentially be applied to the following utility waste streams:

- Ash pond effluent and overflow,
- Cooling tower blowdown,
- Cleaning wastes,
- Roof and yard drainage,
- Boiler blowdown.

Costs

The costs associated with wastewater treatment by lime precipitation are discussed below. Figures 5-6 and 5-7 present curves for lime precipitation capital costs and operation and

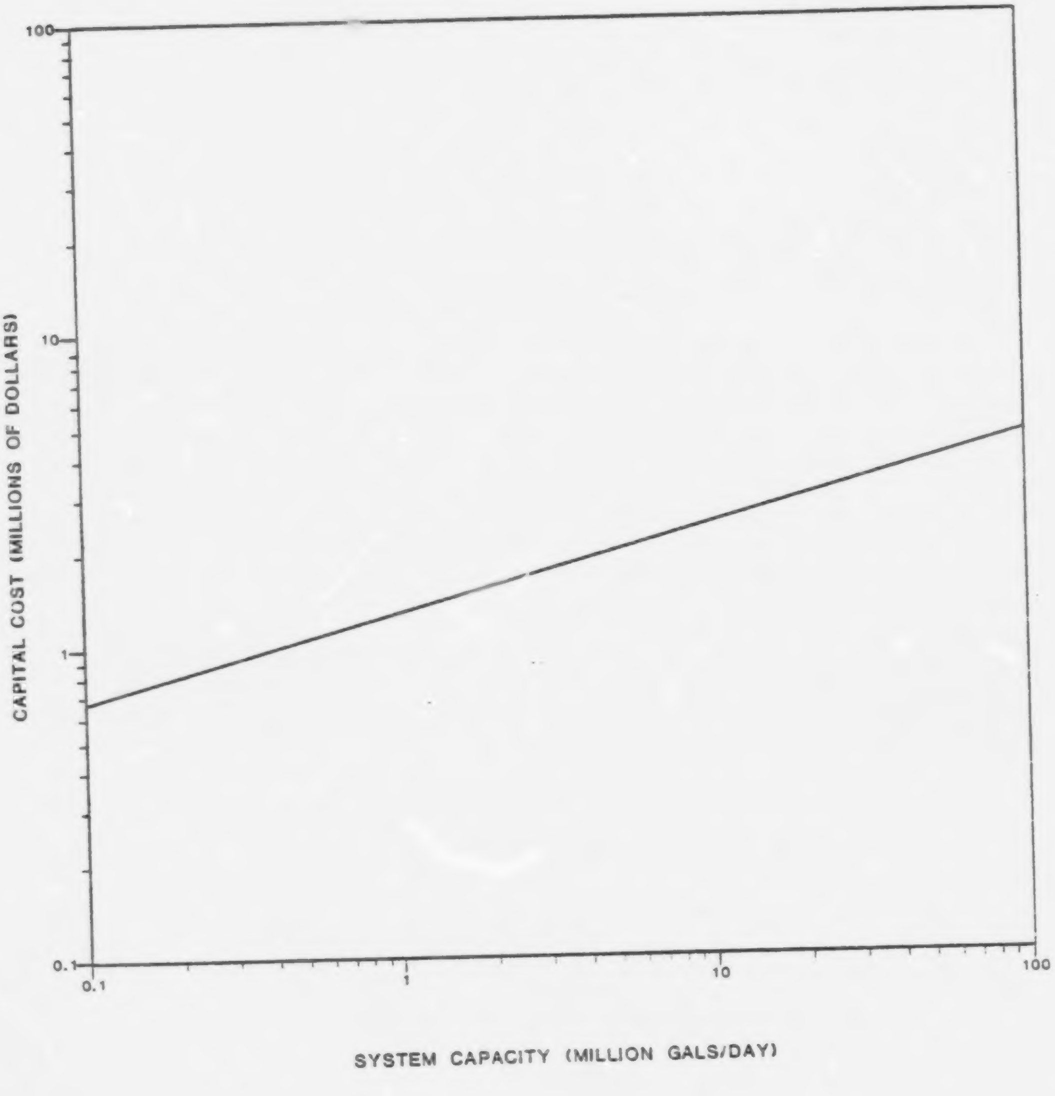


Figure 5-6. Lime precipitation installed capital costs.

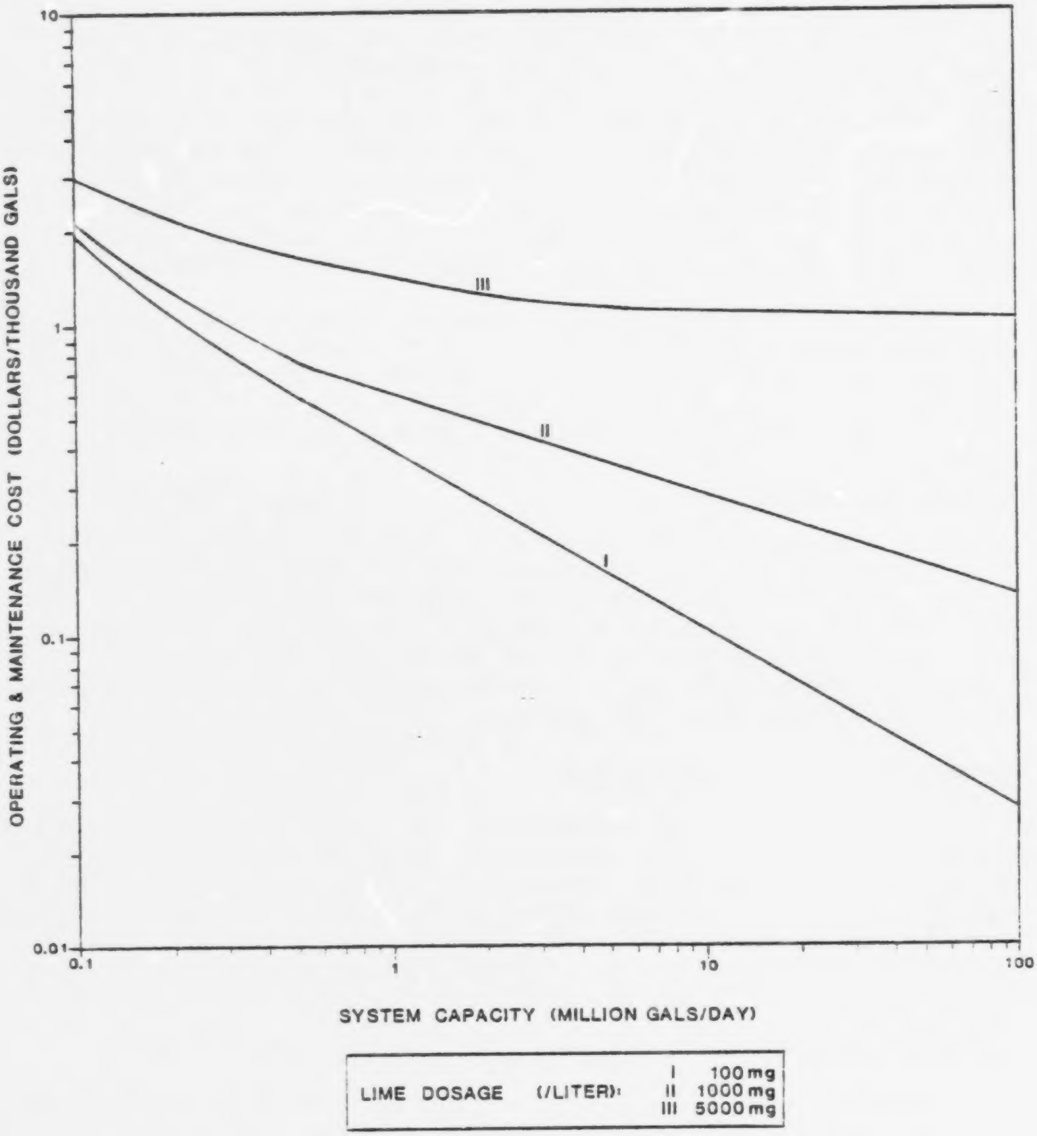


Figure 5-7. Lime precipitation operating and maintenance costs.

maintenance costs. The equipment on which the cost curves are based include a lime feeder, flash mix tank, clarifier/flocculator with sludge recycle, sludge thickener, vacuum belt filter for sludge dewatering, and a filter for final effluent polishing. This equipment selection represents the most capital intensive treatment system. If effluent standards could be met and if land were available, settling ponds and lagoons could be utilized. Capital costs and operating and maintenance costs might be substantially decreased with such an arrangement since it involves less equipment. However, for the application of precipitation for metals removal, the low concentrations may require the more expensive arrangement to obtain adequate overall removals. The costs in Figures 5-6 and 5-7 do not include the costs of disposing of the dewatered sludge. The discussion on solid waste disposal presents these costs later in this section.

The effect of different lime requirements on the operating and maintenance costs due to varying inlet stream alkalinity, pH, and metals concentration is shown in Figure 5-6. Curve I represents a lime dosage of 100 mg/ℓ. Curve II is for a dosage of 1000 mg/ℓ and Curve III for a dosage of 5000 mg/ℓ.

Energy Requirements

The energy requirements for lime precipitation include those for operating the lime feeders, wastewater pumps, clarifier agitator drive, sludge rake drive, and the vacuum filter. For a 500,000 gpd system with a 100 mg/ℓ lime dosage, the energy rerequirement is estimated to be about 8 kW-hrs per 1000 gallons treated. For a 1500 mg/ℓ lime dosage, the energy requirement is about 14 kW-hrs per 1000 gallons.

Secondary Process Emissions

The precipitated solids formed in the clarifier represent a secondary waste when separated from the wastewater. The sludge is usually processed by dewatering in a thickener and vacuum filter to reduce its volume prior to disposal. However, if land is available, it may be sent directly to ponds for disposal. Care must be exercised to prevent the priority pollutants from being leached or discharged from disposal sites or ponds.

REVERSE OSMOSIS

Turnkey reverse osmosis processes are commercially marketed by a number of companies. Reverse osmosis units have been used to treat cooling tower blowdown water to recover water for reuse. Reverse osmosis has also been used to produce drinking water from both sea water and inland brackish water.

Reverse osmosis and electrodialysis produce similar results for water treatment applications and have been used industrially for similar situations. The costs and applications of the two systems are similar. Reverse osmosis will be more effective in reducing non-polar priority pollutants. As a result, only reverse osmosis will be discussed in this section.

Process Description

Reverse osmosis processes utilize semipermeable membranes to purify water. Using pressure as a driving force, water is forced through a membrane resulting in a deionized water and a brine concentrate. The net driving force for flow through the membrane in a reverse osmosis system is the total applied pressure less the osmotic pressure of the system. In general the osmotic pressure of a solution is approximately 0.068 atm (1 psi) for each 100 mg/ℓ of dissolved salt concentration (LY-006).

A schematic flow diagram of a typical reverse osmosis plant is presented in Figure 5-8. The heart of the plant is a semipermeable membrane system and a high pressure pump. Auxiliary systems for handling and processing the feedwater makeup to the process, the purified product water, and the concentrated waste are also important to the plant's operation.

Membrane Development--

Semipermeable membranes used in reverse osmosis processes are all very similar. Although there are many inorganic and synthetic organic materials that possess the property of semipermeability, cellulose acetate is the most common membrane material employed (GI-009). Nylon aromatic polyamide membranes are also used in selected membrane systems (LY-006). The cellulose acetate membranes are approximately 100 microns thick.

Two performance parameters by which reverse osmosis membranes are commonly judged are (1) the rate of water flux through the membrane and (2) salt rejection. These parameters indicate the membrane's permeability to water and to dissolved impurities, respectively. Conventional cellulose acetate membranes achieve maximum water flux rates of 0.0035 to 0.0088 m^3/day/m^2 (10 to 25 gal/day/ft) when desalting water of intermediate salinity (approximately 5000 mg/ℓ TDS). Approximately 90-98% rejection of the salts in the feed stream can be achieved (LY-006). Flux rate and salt rejection are related to membrane parameters and are not independent of each other. "Tight" membranes are characteristic of high salt rejection but they produce the lowest rate of water flux through the membrane. Conversely, "loose" membranes achieve low salt rejection but have high rates

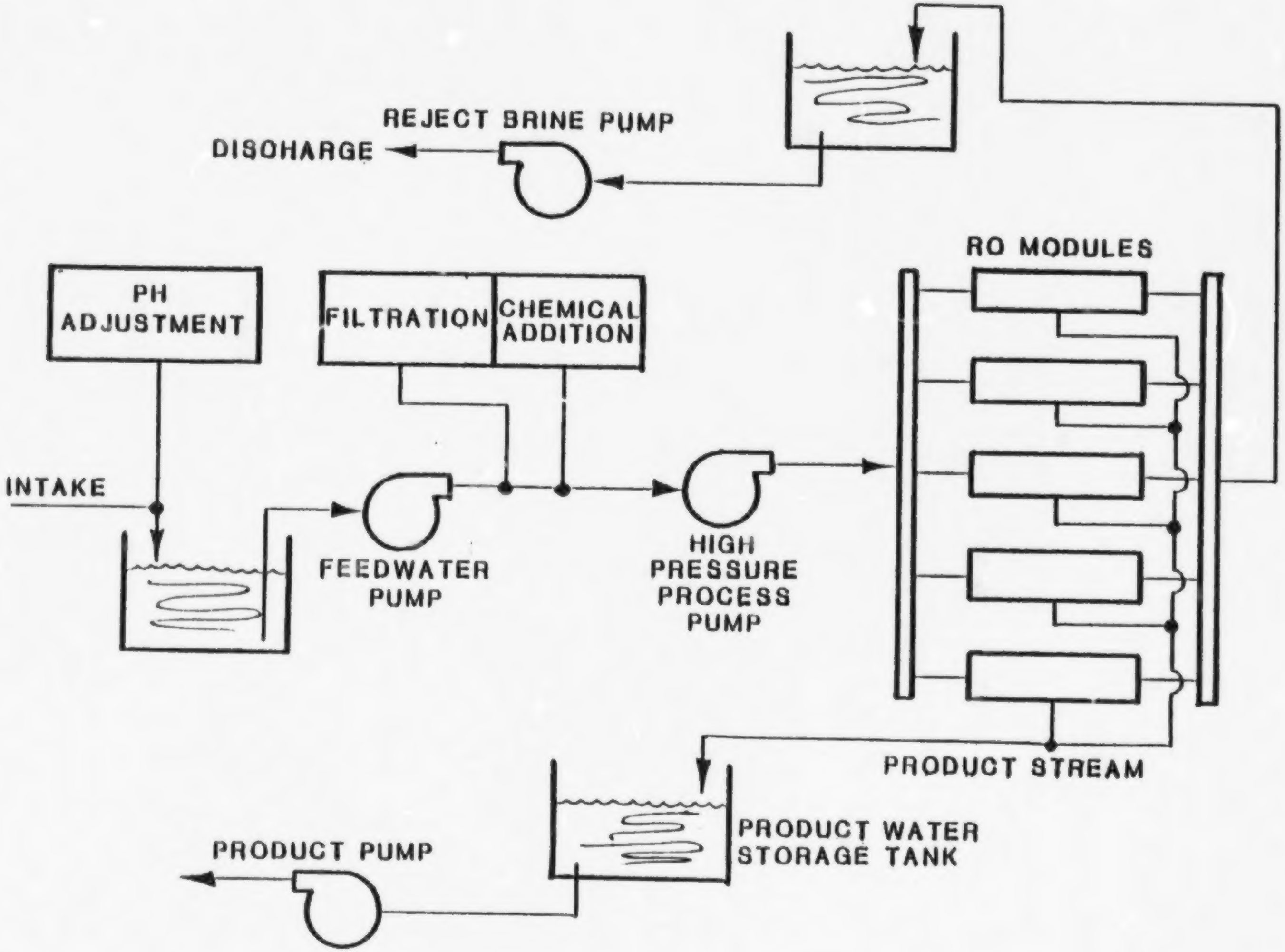

REJECT BRINE PUMP
DISCHARGE
PH ADJUSTMENT
FILTRATION
CHEMICAL ADDITION
RO MODULES
INTAKE
FEEDWATER PUMP
HIGH PRESSURE PROCESS PUMP
PRODUCT STREAM
PRODUCT WATER STORAGE TANK
PRODUCT PUMP

Figure 5-8. Typical reverse osmosis plant arrangement.
Source: HI-041

of water flux (CL-037). Membranes with a broad range of salt rejection parameters and corresponding flux rates can be prepared and are commercially available. The maximum feedwater salt concentration that can be tolerated is reported to range from 5.0 to 50.0 x 10^3 mg/ℓ (LY-006, PA-120).

Membrane Configurations--

Although basically the same type of membrane is used for all reverse osmosis plants, significant variations exist for the membrane configuration that is employed. Configuration in relation to reverse osmosis systems refers to the membrane supporting mechanism. The basic configurations available are:

- plate and frame
- tubular
- spiral wound
- hollow fine fiber

Membrane Fouling--

Reverse osmosis membranes are subject to fouling from any number of many different fouling agents. The most significant of these agents are:

- biological growths
- suspended solids or particulate matter
- scale
- manganese and iron
- organics

To control membrane fouling, a feedwater pretreatment step is often dictated and certain limitations are imposed on the process. Process feed pretreatment can take several forms depending upon each particular feedwater, i.e., softening and filtration.

In addition to pretreatment, scale control also imposes restrictions or limitations on the reverse osmosis process. Scale formation is driven by supersaturation of a solution with respect to a chemical salt. Calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4$), and magnesium hydroxide [$Mg(OH)_2$] are the primary scaling salts due to their low solubilities. Therefore, these salts must be kept below their saturation concentrations in order to avoid precipitation and scale formation. The conversion of saline water to desalted water by reverse osmosis is obviously limited by the feedwater concentration that can be achieved. The degree of concentration varies with the quality of feedwater to the process.

A scaling problem that sometimes occurs in the reverse osmosis process is attributed to concentration polarization. This phenomenon results from inadequate mixing of the saline water layer adjacent to the membrane's surface with the bulk of the saline water concentrate. Localized supersaturations can occur in this water layer even though the bulk waste stream remains subsaturated. Concentration polarization is minimized by proper hydrodynamic control of the concentrate stream.

Membrane Life--

The service life of a reverse osmosis membrane is determined by its ability to maintain water flux rates and salt rejection characteristics. Significant reduction in either performance parameter below prescribed levels is grounds for removing a membrane from service. The maximum life expectancy of cellulose acetate membranes ranges from 1 to 2 years. Nylon fiber membranes have a maximum service range of approximately 3 years.

The water flux rate and salt rejection properties of cellulose acetate membranes are significantly affected by membrane compaction and membrane hydrolysis, respectively. Compaction refers to the physical crushing of a membrane's porous structure. Subjection to extended periods of high hydraulic pressure causes compaction. As the degree of compaction becomes more severe, the rate of water flux through a membrane continually decreases. A maximum operating pressure of approximately 40-50 atm (600-800 psi) is generally adopted for cellulose acetate membranes (LY-006). Higher pressures accelerate the rate of membrane compaction without producing significantly higher rates of water flux (GI-019). The membranes are periodically backflushed to remove any plugging or fouling that might have occurred. The backflush stream is usually routed to the reject brine stream.

Hydrolysis refers to the chemical reaction that occurs between membrane material and water. Hydrolysis results in a deterioration of salt rejection properties for the membrane. Feedwater temperature and pH influence the rate of membrane hydrolysis. They are important operating parameters to control in extending membrane life. Cellulose acetate membranes have a maximum temperature limitation of 40°C (100°F). The hydrolysis rate for these membranes significantly increases at higher operating temperatures. The pH range suggested for cellulose acetate membranes is 3 to 8 (GO-063). Nylon membranes used in hollow fine fiber modules can withstand more severe pH extremes; pH values of 1.5 to 12.0 can be tolerated (GO-063). Thus, the nylon fibers give more operating flexibility with respect to pH. For certain membranes, chlorine concentrations greater than 0.1 ppm significantly reduce membrane life (PR-166).

Control Effectiveness

Reverse osmosis units have typically demonstrated 90-98% salt rejection for feedwater with dissolved solids as high as 12,000 ppm. This results in product water TDS levels of about 200 ppm with 75% water recovery with one stage. Multiple stage reverse osmosis systems can be used to achieve product TDS levels as low as 50 ppm. The metallic priority pollutants generally are reduced as the TDS is lowered. Also, reverse osmosis will remove more than 95% of organics and all colloidal particles down to 0.05 microns (DI-149). Reverse osmosis could be applied to all waste streams from the electric utilities except cleaning water because of pH considerations and lab drains because of high organic concentrations. Reverse osmosis would probably not be used alone to treat streams to remove priority pollutants because of the large volume of the waste stream. For example, reverse osmosis could be used as a pretreatment with its reject brine sent to a vapor compression distillation unit.

Costs

The major factors influencing the cost of a reverse osmosis unit are the feedwater rate, membrane replacement costs, and the number of stages employed. The concentration of the priority pollutants should not significantly effect reverse osmosis costs.

Listed in Table 5-3 are cost data for reverse osmosis water treatment at different system capacities. These data are based upon TDS of 3000 ppm and purified water TDS of 50 ppm with 80% recovery of water (GE-122).

Another vendor (DI-151) reports installed capital costs between $0.80 and $1.00 per gallon per day of water processed for capacities greater than 80,000 gallons per day. These reverse osmosis processes are one stage and provide 98% salt rejection for feedwater up to 12,000 ppm TDS. Operating costs are about $0.75 per 1000 gallons of water processed which included membrane replacement costs.

TABLE 5-3. COST OF WATER TREATMENT BY REVERSE OSMOSIS

System Capacity[1]	10,000 GPD	25,000 GPD	100,000 GPD	500,000 GPD
Capital Cost (Installed)	$20,000	$39,900	$91,000	$365,000
Membrane Cost	2,200	5,500	22,000	110,000
Operating Costs ($/1000 gal)				
Membrane Replacement[2]	0.25	0.25	0.25	0.25
Power (@ $.02¢/kW-hr)	0.34	0.27	0.18	0.17
Labor (@ $10/hr)	1.28	0.51	0.14	0.07
Maintenance and Repairs	0.15	0.12	0.10	0.08
Chemicals and Filters	0.12	0.10	0.08	0.05
Wastewater[3] Disposal	0.04	0.04	0.04	0.04
TOTAL OPERATING COST ($/1000 gal)	$2.18	$1.29	$0.79	$0.66

[1] Assumed Operating Schedule: 85% Service - 350 Days/Year

[2] Assumed 125% Membrane Replacement every three years

[3] At 80% Fractional Recovery and Water Cost of $53/Acre-Foot

Source: MA-693

Figures 5-9 and 5-10 show capital and operating costs, respectively, for a reverse osmosis process as a function of the flow rate. These costs are for single stage reverse osmosis which achieves 75% water recovery and 90-98% salt rejection. With 12,000 ppm TDS feedwater, the product water will have about 500 ppm TDS.

Energy Requirements

The major power consumer in a reverse osmosis unit is the pumps. For 100,000 gpd units and larger, the energy requirements are between 8 and 10 kW-hr/1000 gallon of water processed for one stage. If multiple stage reverse osmosis processes are used, the energy requirements will increase almost directly with the number of stages.

Secondary Process Emissions

The major waste stream from a reverse osmosis unit is the reject brine stream. This stream carries the majority of the dissolved solids brought into the process by the feedstream. This reject brine stream will be a large volume waste stream (~25% of the original stream); therefore, reverse osmosis can be used to concentrate toxic species to make other controls less expensive and more effective.

DEEP BED FILTERS

Turnkey deep bed filters are commercially available. Deep bed filters have been used by many industries, including the electric utility industry, which uses these filters to remove suspended solids from effluent streams. Deep bed filters would be used only as a pretreatment step to remove suspended solids prior to priority pollutant control technologies.

Process Description

Deep bed filters utilize a bed of granular filter medium to separate suspended matter from an aqueous solution. The beds are usually arranged with the smaller particle size filter media at the inlet side of the filter bed and the larger particle size media at the end of the filter bed. Accumulation of suspended matter within the filter media increases the bed's resistance to liquid flow. When the pressure drop across the bed becomes excessive, the filter bed must be regenerated. Regeneration is usually accomplished by backwashing the filter. Feedwater flows to conventional sand filters range from 0.07 to 0.14 $m^2/min/m^3$ of filter cross-sectional area (2 to 4 gpm/ft^2).

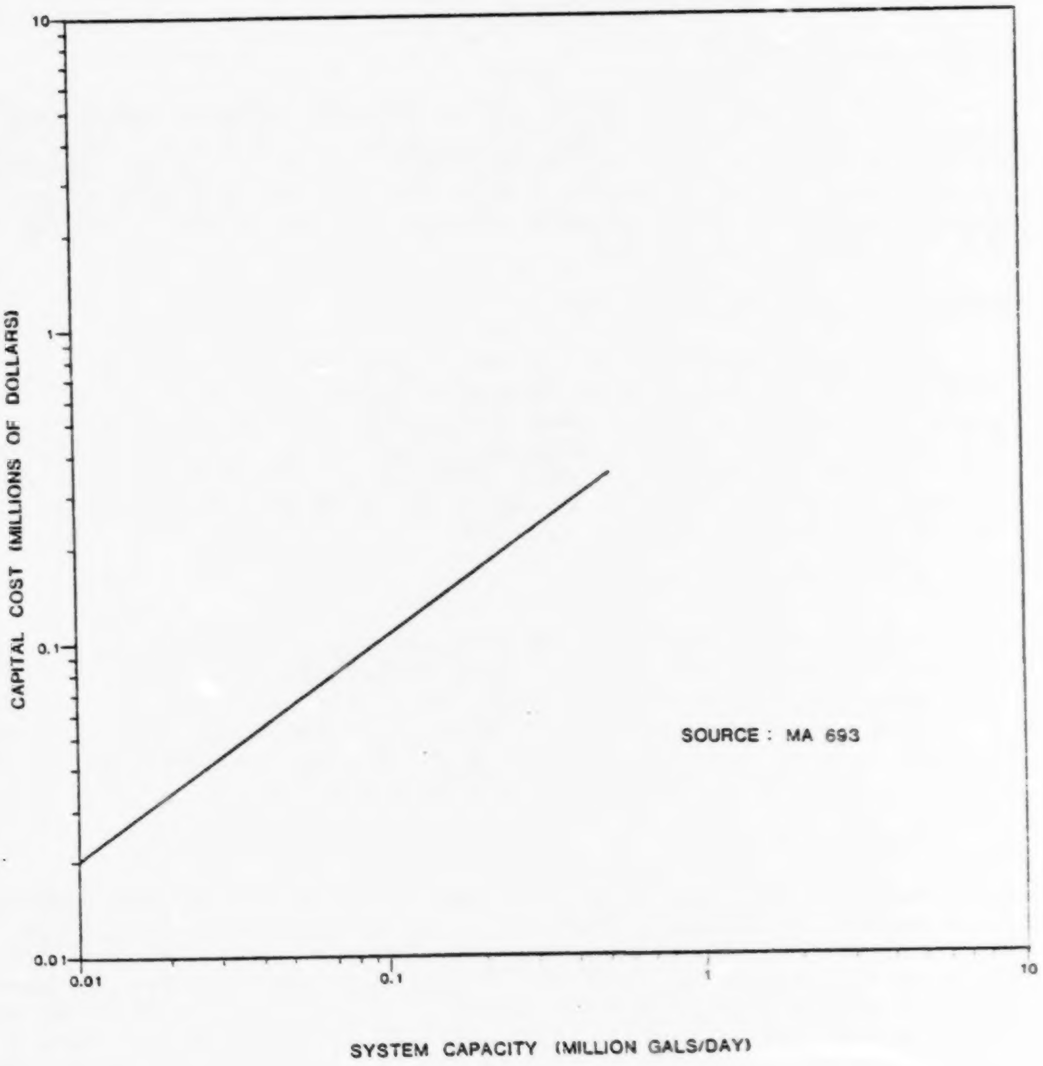


Figure 5-9. Capital costs for reverse osmosis.

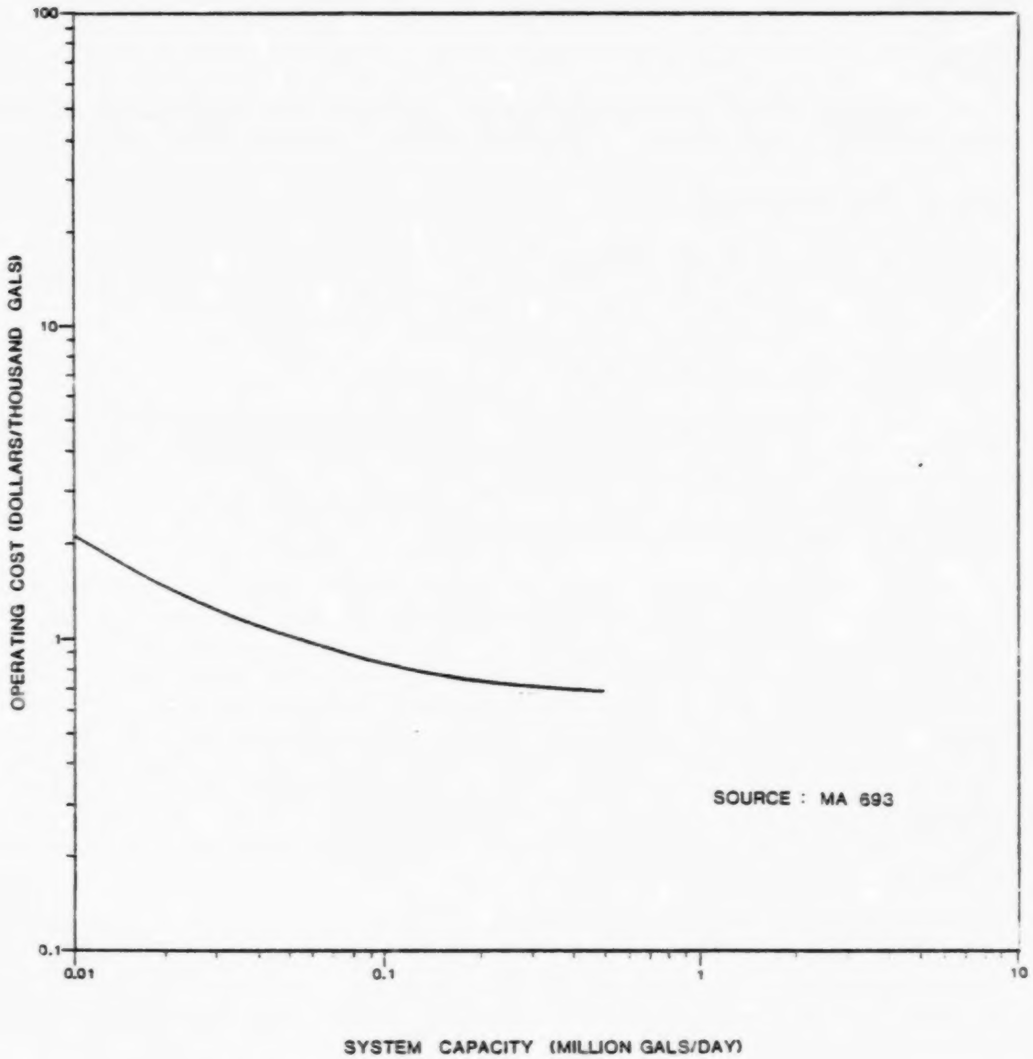


Figure 5-10. Operating costs for reverse osmosis.

Control Effectiveness

Deep bed filters remove suspended solids in the particle size range of 0.1 to 50μ. These filters can be applied to treat dilute suspensions containing up to 1000 mg/ℓ of suspended matter.

Costs

Figures 5-11 and 5-12 shows capital and operating costs for conventional sand or graded media filters (SM-176).

Energy Requirements

The only energy requirements would be for pumping the solution through the filter. The energy requirements should be in the range of 0.3 to 0.5 kW-hr/1000 gallon.

Secondary Process Emissions

The filter backwash which is produced during filter regeneration is a waste stream from a deep bed filter. This stream can be sent to a settling pond.

VAPOR COMPRESSION DISTILLATION

Vapor compression distillation (VCD) can be used to treat and recover water from the continuous waste streams of an electric-power generating station. The process produces a high quality water stream while concentrating the dissolved solids in a slurry of about 10% the original stream volume (RE-259). Thus, VCD processes can be used to concentrate non-volatile effluents from steam-electric utilities into a stream which can be more easily treated. The concentrated reject brine stream is usually ponded in arid regions. For non-arid regions, the brine stream is either sent to an ash pond or treated with a vaporization crystallizer.

Turnkey VCD processes have been commercially available for over ten years. VCD processes have been installed in electric power generating stations in the western and southwestern states to recover deionized water from cooling tower blowdown (LE-299).

Process Description

Figure 5-13 shows the flow diagram for a VCD unit. The water stream is first treated in a feed tank to adjust the pH to between 5.5 and 6.5 for decarbonation. The waste stream is then pumped through a heat exchanger to raise its temperature to the boiling point. Softening may be required to prevent scaling

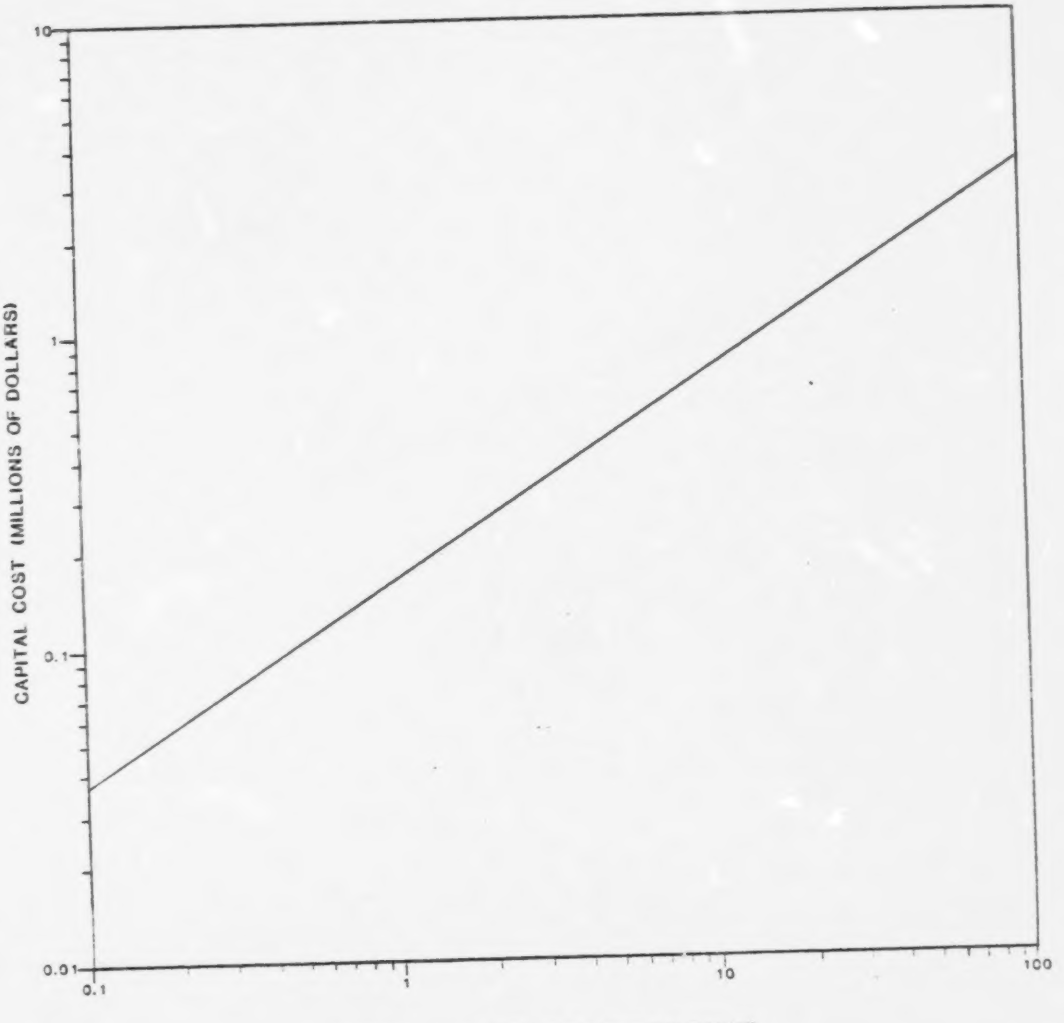


Figure 5-11. Capital costs for conventional sand or graded media filters.

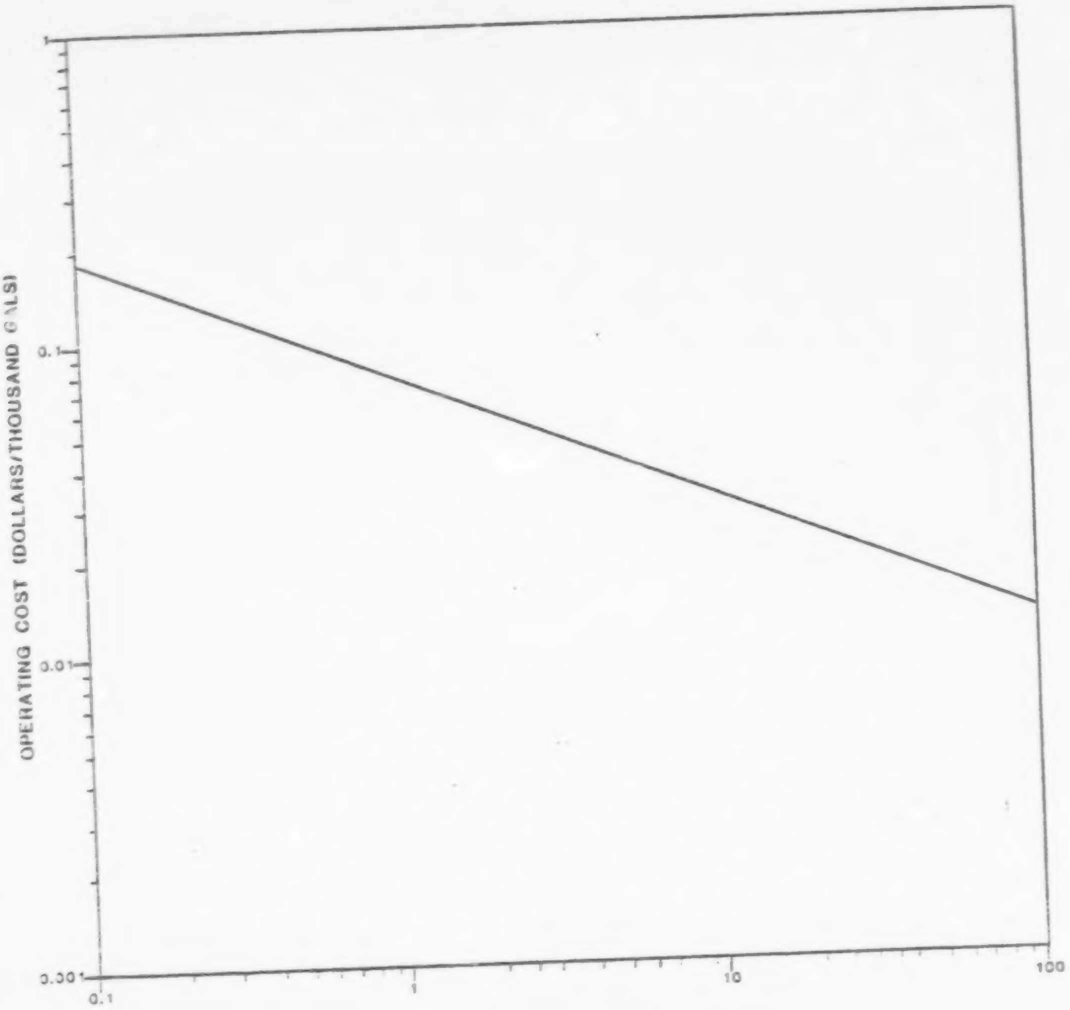


Figure 5-12. Operating costs for conventional sand or graded media filters.

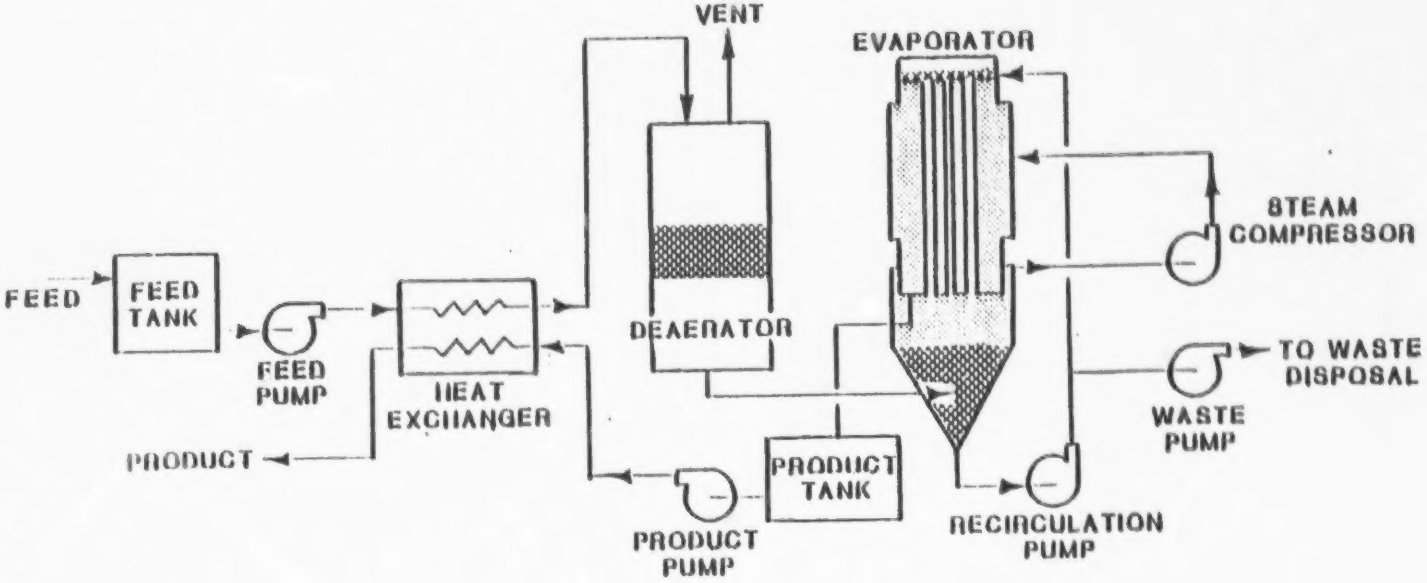

FEED
FEED TANK
FEED PUMP
HEAT EXCHANGER
PRODUCT
VENT
DEAERATOR
PRODUCT PUMP
PRODUCT TANK
EVAPORATOR
STEAM COMPRESSOR
TO WASTE DISPOSAL
WASTE PUMP
RECIRCULATION PUMP

Figure 5-13. VCD simplified system schematic.

Source: RE-259

in the heat exchanger. After passing through a deaerator to remove dissolved gases, the hot waste stream is combined with the slurry concentrate in the evaporator sump. The brine slurry is constantly circulated from the sump to the top of the evaporator tubes. The slurry flows as a film on the inside of the tubes down to the sump. As the slurry falls down through the tubes, part of the slurry water is vaporized by the steam condensing on the outside of the tubes. This vapor is compressed and introduced to the shell side of the tube bundle. As this stream condenses, it returns its heat of vaporization to the brine slurry. This condensate (<10 ppm TDS) is pumped through the feed preheater to return as much heat as possible to the process before it is recycled to the plant for reuse. The brine slurry is continuously removed from the sump to maintain constant slurry concentration. The waste brine can be sent to a pond or mechanical drying system for final disposal.

The VCD process is able to avoid scale formation on heat transfer surfaces by preferential precipitation of calcium sulfate and silica on seed crystals in the slurry. Also, a small temperature difference across the heat transfer tubes is maintained to minimize scale formation on the evaporating surfaces.

The VCD unit is constructed of corrosion-resistant materials: titanium, stainless steel, and special steel alloys. Inspection of corrosion levels in existing facilities indicated that the designed 30-year life of the equipment should be achieved. A 95% service factor has been observed (LE-299).

Control Effectiveness

VCD units have taken inlet waters with 10,000 ppm TDS and produced a condensate stream with less than 10 ppm TDS while recovering approximately 90% of the water (RE-259). Therefore, non-volatile and organic metal species should also be reduced by about the same proportions as TDS. VCD processes can be applied to all utility wastewater streams except streams containing a significant level of organic compounds.

VCD has been applied to cooling tower blowdown in the electric utility industry with the product water returned to the plant for reuse as cooling tower makeup water and boiler feed water.

If significant amounts of priority pollutants are vented from the deaerator, some control process (such as carbon adsorption) may be required on the vent.

Costs

The basis of the cost data (LE-299) for a turnkey vapor compression distillation unit assumes 90% water recovery for a waste stream containing 10,000 ppm TDS producing a purified condensate (<10 ppm TDS). Two sizes are available on the market from one vendor and cost data for these sizes are presented in Table 5-4. The cost data does not include the cost for the disposal of the waste brine.

TABLE 5-4. CAPITAL AND O/M COSTS FOR VAPOR COMPRESSION DISTILLATION

	216,000 gpd	432,000 gpd
Vendor A (LE-299)		
Capital Cost (installed)	$2,000,000	$3,700,000
O/M	$1.8-2.0/1000 gal	$1.8-2.0/1000 gal
Vendor B (BO-290)		
Capital Cost (installed)	$1,500,000	$2,800,000
O/M	$1.8-2.0/1000 gal	$1.8-2.0/1000 gal

Another vendor (BO-290) offers a VCD unit which has the same specifications as a brine concentrator for about three-fourths the capital costs with comparable O/M costs as shown in Table 5-4.

Because of the large capital costs for relatively low treatment water rates and the high operating costs, it is probably more cost effective to have a VCD unit preceded by a pretreatment process, i.e., reverse osmosis. A reverse osmosis unit would reduce the volume of water to be treated by about 75% at a much lower cost than if VCD were used to treat it.

Energy Requirements

VCD units are very energy intensive processes requiring approximately 90 kW-hr/1000 gallon of water processed (RE-259). Almost all this energy goes into driving the electric vapor compressor. It is possible that steam-driven vapor compressors would have certain economic advantages if low cost waste steam were available. The concentration of priority pollutants do not affect the energy requirements.

Secondary Process Emissions

The major waste stream from a VCD process is the waste brine concentrate slurry. This stream carries the majority of the dissolved solids brought into the process by the feedwater. This reject brine stream is usually ponded. Costs should be charged for the disposal of this waste stream. In nonarid regions, significantly more disposal costs may result. A vaporization crystallizer, which is a very energy intensive process, may be required in certain nonarid regions to dispose of the waste brine slurry.

The dearator also produces a gaseous stream which is vented. This stream will contain mostly CO_2, N_2, and O_2. If there are volatile pollutants in the feed, they may be flashed and vented by the aerator.

EVAPORATION PONDS

Evaporation ponds use solar energy to evaporate water from plant waste streams and thus, collect, concentrate, and precipitate dissolved solids in the waste streams. These precipitated dissolved solids are usually allowed to accumulate on the bottom of the pond or, in some instances, are periodically dredged from the pond.

Evaporation ponds have been used throughout the chemical industry and the electric utility industry. Evaporation ponds may be required to be lined to prevent seepage of dissolved chemicals into underground water supplies. Evaporation ponds can be constructed by excavating the pond, enclosing an area with dikes, building a dam, or a combination of these methods.

The applicability of evaporation ponds depends upon the net evaporation rate, i.e., the gross evaporation rate minus rainfall. Geographical areas with less than 50 cm (20 in.) net annual evaporation rate should not be considered for evaporation pond use. Land must be available where the evaporation pond can be built. Low cost land is desirable. The difficulty in excavation of the land is also a factor. Finally, local regulations must permit the use of such ponds.

Process Description

Solar evaporation may be performed in a single pond or in a series of ponds. A graduated increase in brine salinity is obtained by evaporation ponds in series. Chemical salts with lower solubilities precipitate in the first ponds while more soluble salts precipitate in latter ponds. As the salinity increases, the pond evaporation rates decrease due to effects on the partial vapor pressure of water.

The area required for a single evaporation pond which evaporates G gallons/minute is given by

$$\text{Area (Acres)} = \frac{19.5G}{V} \qquad (5\text{-}1)$$

where V is the effective net evaporation rate (inches/year). The effective net evaporation rate is less than the net evaporation rate due to the reduction of the water vapor pressure that is caused by the dissolved salts in the water in evaporation ponds. Some experimental evidence (FO-130) indicates that the effective net evaporation rate is in the range of 50% to 70% of the net evaporation rate.

Control Effectiveness

All streams could be potentially controlled by evaporation ponds, but land availability and evaporation rate limit high flow rate streams from being discharged to a pond. The major limitations to the control effectiveness of evaporation ponds in arid regions is the problem of seepage of pollutants into underground water supplies. Even with the most carefully designed lined evaporation pond, the possibility exists that the lining may rupture. There is also the question as to the effectiveness of pond liners. Additional experimental work is needed to adequately determine their permeabilities.

Costs

In Figures 5-14 and 5-15, capital and operating costs of evaporation ponds are shown as a function of water rate to the pond with the effective net evaporation rate as a parameter. The effective net evaporation rate is less than the net evaporation rate due to the reduction of the water vapor pressure that results from the dissolved salts in the water in evaporation ponds. The capital cost figure is based upon assuming \$2/cubic yard of land moved to form a 4 foot high dike with a 27 foot base. It is also assumed that the pond liner costs \$0.25/ft^2 and land costs \$1000/acre. The cost of excavation ranges from \$2 to \$6/cubic yard depending upon the type of land to be excavated. Liner costs range from \$0.20 to \$0.40/ft^2 depending upon the type and thickeness of liner used. Land costs can range anywhere from \$200/acre to \$10,000/acre or more. The operating costs are for pumping and dike area maintenance.

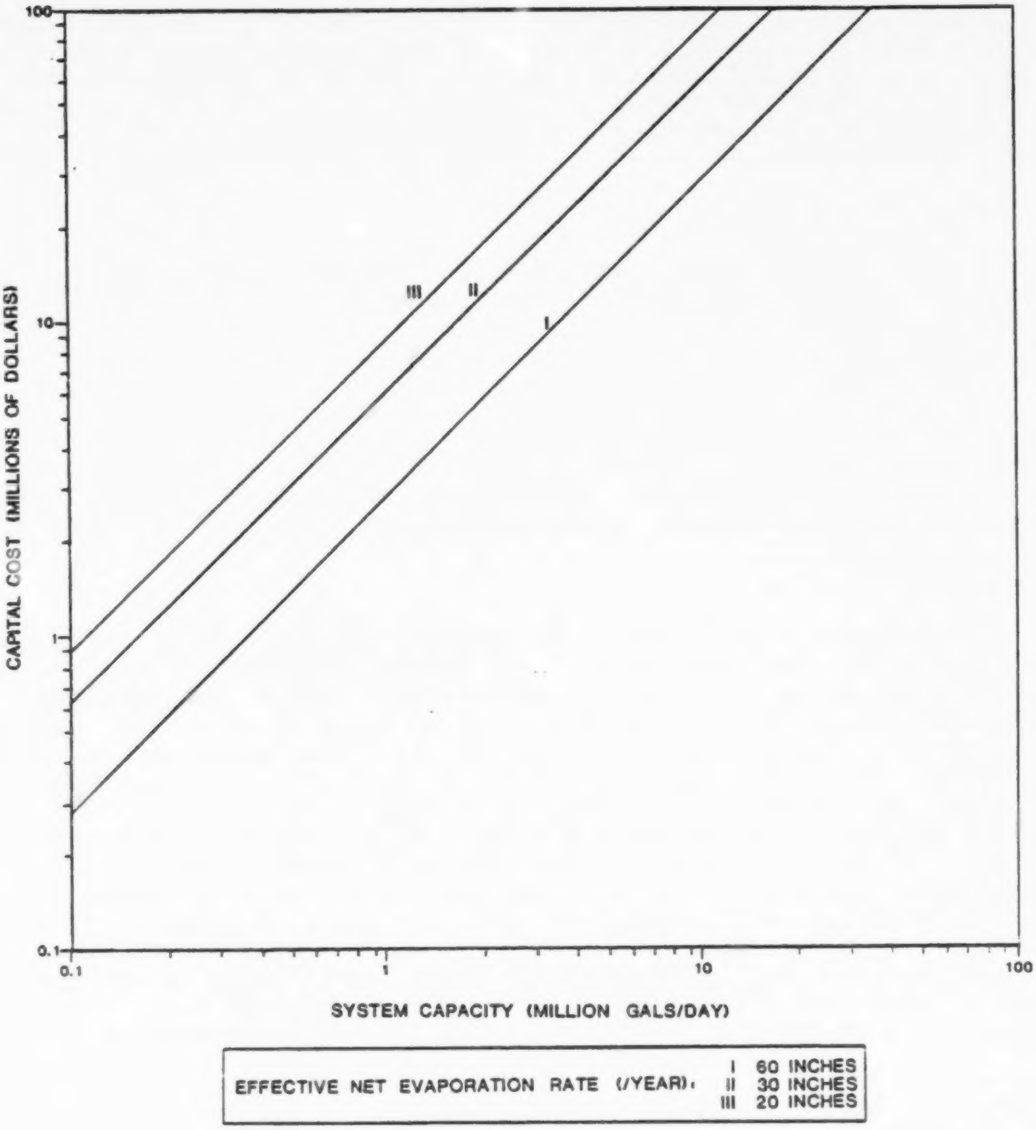


Figure 5-14. Capital costs for evaporation ponds.

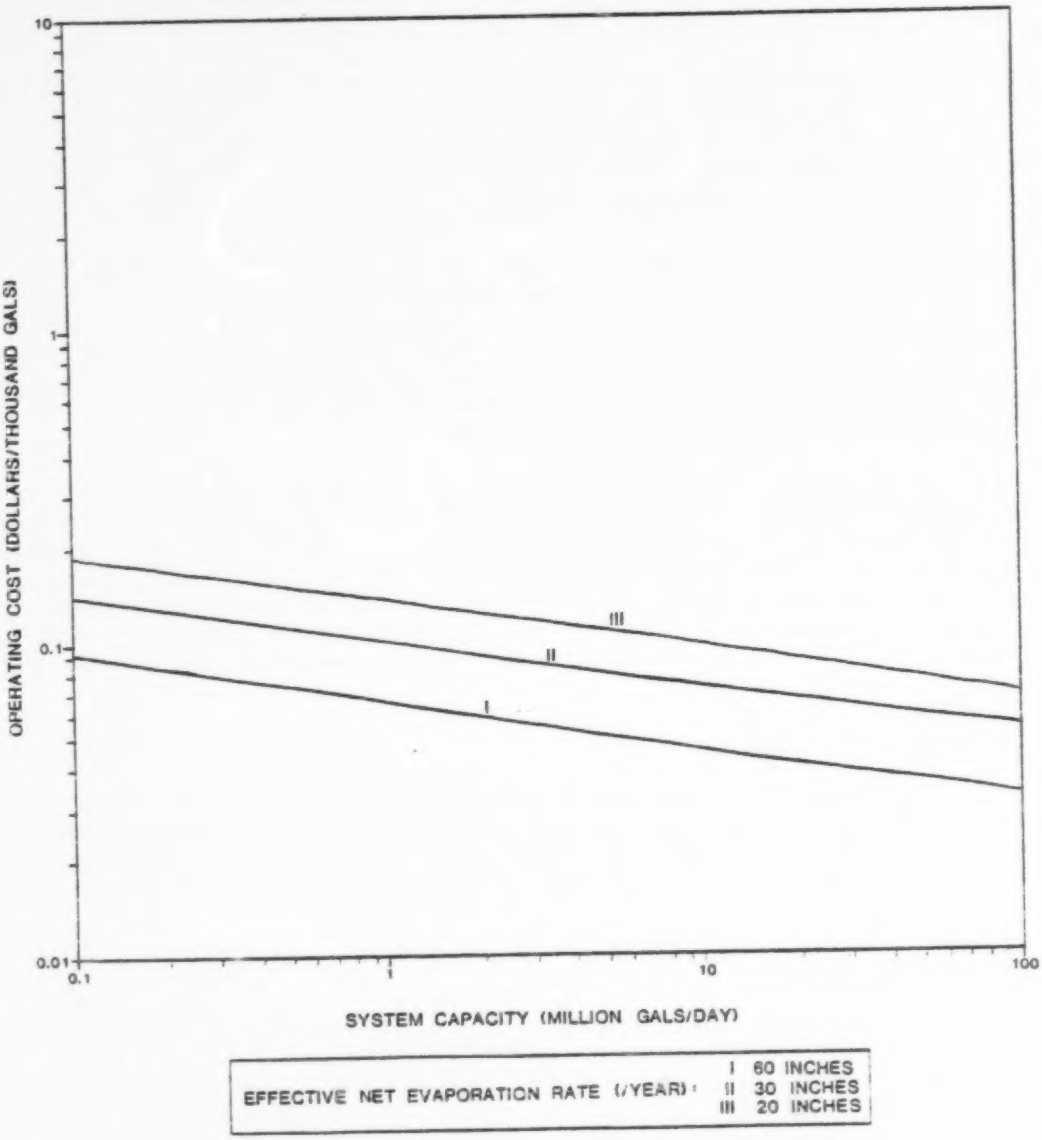


Figure 5-15. Evaporation pond operating costs.

As an example of the cost breakdown, consider a 150 gpm ash pond overflow rate for a utility located in a region where the effective net evaporation rate is 30 inches/year. From Equation 5-1, the pond area required to evaporate 150 gpm is 97.5 acres. The installed capital costs of this evaporation pond with a dike having a cross section shown in Figure 5-16 (A) is:

Land cost ($1000/acre)	$ 100,000
Excavation and building dikes	$ 45,000
3-inch thick asphalt liner	$1,060,000
Pumps and lines (installed)	$ 10,000
TOTAL INSTALLED COSTS	$1,215,000

The 3-inch thick asphalt liner costs approximately 25¢/ft^2 (FO-130). The excavation and dike building costs were calculated assuming $2/cubic yard of land moved to form the dike. If the land is not easily excavated, the cost will significantly increase. The operating costs are estimated to be 12¢/1000 gallons treated assuming that the solids can be allowed to accumulate on the bottom of the pond.

A western utility (FO-130) reported building three 20-acre evaporation ponds to evaporate 300 gpm (an effective net evaporation rate of 97 inches/year) at a cost of $1,550,000 excluding land costs. The ponds were lined with 3-inch thick asphalt, AS 4000, using a prime coat of MC250 (FO-130). This liner was chosen because of its superior resistance to seepage. Each pond has a 14-foot high dike with the cross section as shown in Figure 5-16 (B).

Energy Requirements

The major energy requirements for evaporation ponds are for pumping the stream to the pond. The energy requirements for pumping a distance of 1000 feet at a rate of 150 gpm is about 0.5 kW-hr/1000 gallons based upon a 5 feet/second flow velocity.

Secondary Process Emissions

If the pond is designed for solids settling and is designed to eiminate seepage, there should be no process emissions from an evaporation pond except for the potential evaporation of volatile compounds to the atmosphere. If the pond is periodically dredged, a disposal of solid waste is required.

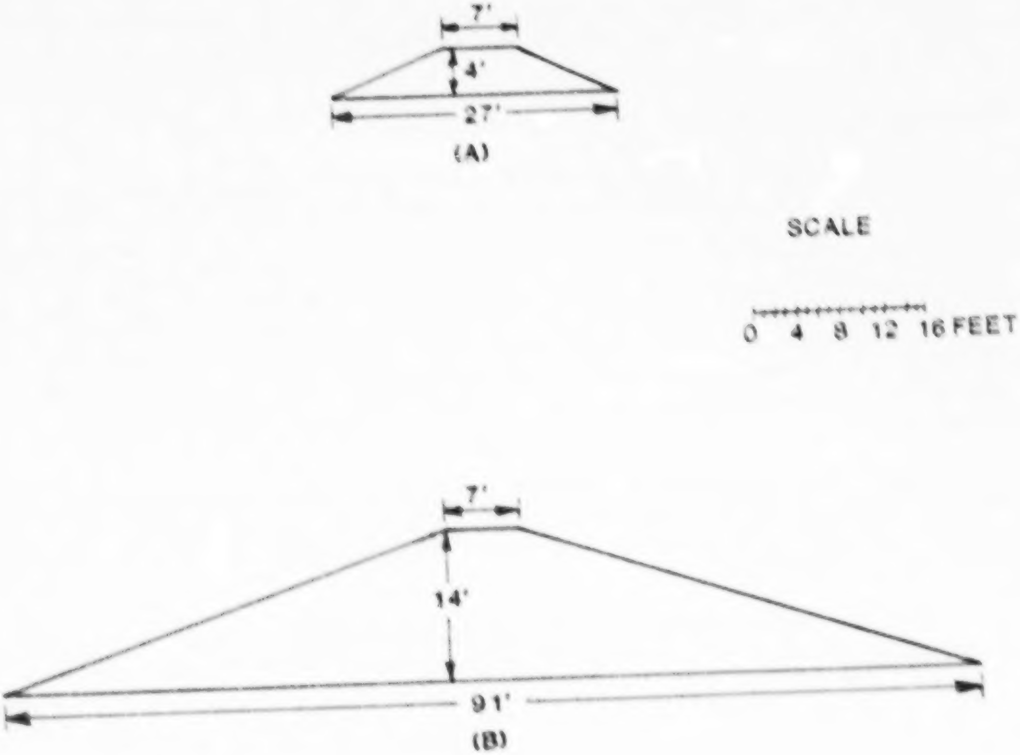

7'
4'
27'
(A)
SCALE
0 4 8 12 16 FEET
7'
14'
91'
(B)

Figure 5-16. Dike cross-sections.

SOLID WASTE DISPOSAL

Solid waste disposal is discussed here as a means of controlling secondary solid wastes resulting from control technologies. Solid wastes can result from treatment of wastewater by precipitation, carbon adsorption, or vapor compression distillation. It is not presented as a primary effluent control technology.

Process Description

The sludge resulting from lime precipitation can be ponded or possibly chemically fixed and used as a landfill. When ponds are used, they are usually required to be lined to prevent seepage into underground water supplies. Lining the pond is usually not necessary when the pond bottom is composed of clay and is at least a couple of feet in thickness. Chemical fixing involves adding chemicals (e.g., fly ash and lime) to solid wastes which results in cement reactions which render the mixture a strong, relatively impermeable solid. This solid is well suited for landfill.

When the activated carbon from a carbon adsorption process is not regenerated, the spent carbon must be disposed of. The carbon can be mixed with the coal and burned in the boiler or used in a landfill.

Vapor compression distillation produces a brine slurry that must be disposed of. This slurry can be sent to an evaporation pond or the water can be removed from the slurry and the remaining solid used as landfill or placed in a lined pond. Deep well disposal may also be a possibility for disposal of this brine slurry.

Control Effectiveness

Data is generally unavailable on the effectiveness of solid waste disposal on priority pollutants. Loss of effectiveness of solid waste disposal can occur due to seepage of water entrained with the solids. Rain run-off can also be a problem.

Costs

Very little information is available for the disposal costs of these three different solid wastes. An example of solid waste disposal costs is presented with cost data for the disposal of flue gas desulfurization sludge and fly ash. These costs are reported in terms of dollars per dry ton of solid.

Disposal Method	$/dry ton of solid wastes (LE-278)
Lined Pond	6.4 to 8.8
Chemical Treatment	8.2 to 12.8

The basis for these costs are:

- 1000 MW power plant producing sludge at a rate of 125 tons/day on a dry basis
- transporting the solid waste 5 miles from the power plant

The annualized costs include the cost of labor, maintenance, and capital costs of 18 percent.

Energy Requirements

The only energy requirements are for pumping or hauling the solid wastes to the disposal site. The energy requirements are highly site-specific and depend upon the type of solid waste and the method chosen to dispose of it.

Secondary Emissions

Seepage of the waste liquors into underwater water supplies is a possible emission from solid waste disposal. If organics are present, they may evaporate into the atmosphere.

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APPENDIX A

DISCUSSION OF THE CHARACTERISTICS OF UTILITY POWER PLANTS EFFLUENT STREAMS

The steam-electric power industry uses large quantities of water primarily for cooling purposes. There are, however, several other water utilizing processes most of which produce a wastewater stream. The qualities of the wastewaters from these processes vary over wide ranges depending primarily on intake water quality and/or the characteristics of the power generating facility involved. Generalized descriptions of the water utilizing processes and the wastewater streams associated with them are contained in this section.

Figure A-1 graphically summarizes the sources of wastewater in a fossil-fueled generating station and depicts the interrelation of the various processes producing these waters. The sources of wastewater are:

- cooling water systems,
- boiler water systems,
- ash handling systems,
- coal pile,
- general plant drainage systems,
- process spills and leaks, and
- miscellaneous operations.

Wastewater discharges associated with flue gas scrubbing will not be evaluated in this document.

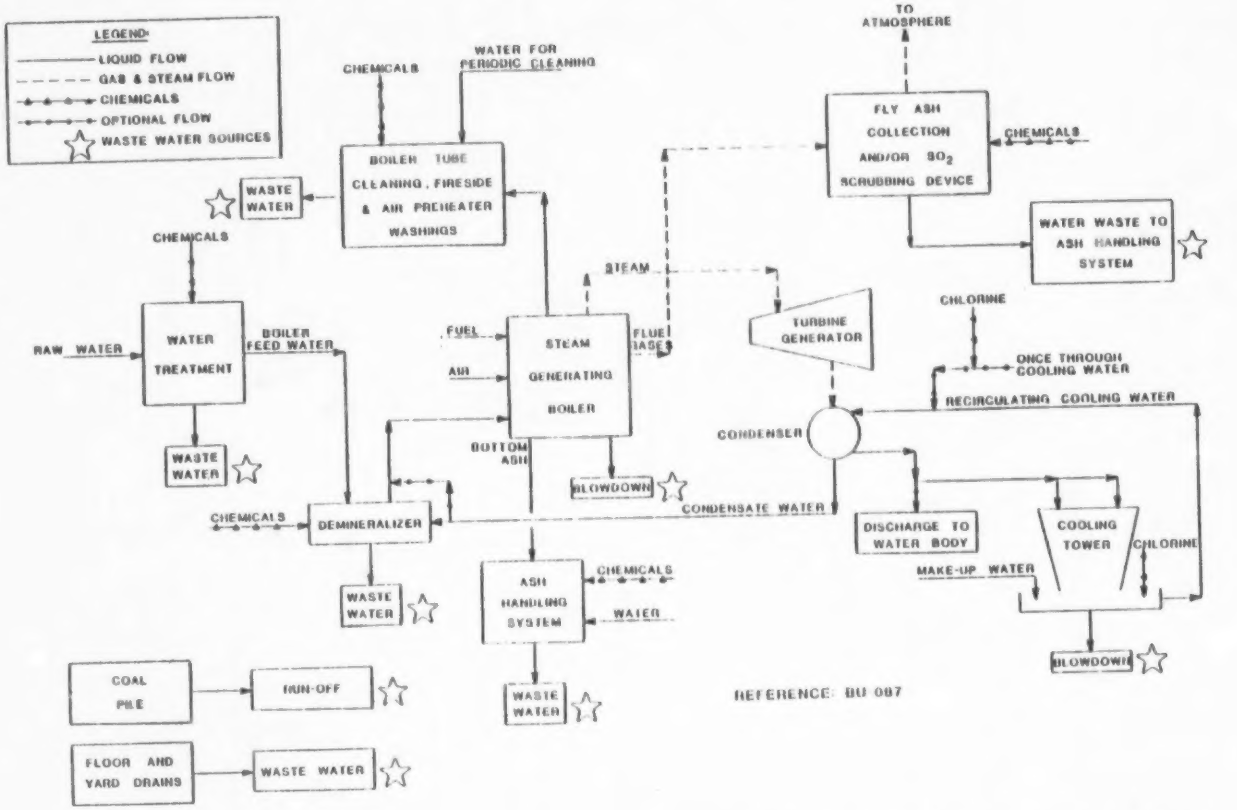

LEGEND:
LIQUID FLOW
GAS & STEAM FLOW
CHEMICALS
OPTIONAL FLOW
WASTE WATER SOURCES
CHEMICALS
WATER FOR PERIODIC CLEANING
BOILER TUBE CLEANING, FIRESIDE & AIR PREHEATER WASHINGS
WASTE WATER
TO ATMOSPHERE
FLY ASH COLLECTION AND/OR SO2 SCRUBBING DEVICE
CHEMICALS
WATER WASTE TO ASH HANDLING SYSTEM
CHEMICALS
RAW WATER
WATER TREATMENT
BOILER FEED WATER
WASTE WATER
STEAM
FUEL
AIR
STEAM GENERATING BOILER
FLUE GASES
BOTTOM ASH
BLOWDOWN
TURBINE GENERATOR
CHLORINE
ONCE THROUGH COOLING WATER
RECIRCULATING COOLING WATER
CONDENSER
CONDENSATE WATER
CHEMICALS
DEMINERALIZER
WASTE WATER
DISCHARGE TO WATER BODY
COOLING TOWER
CHLORINE
MAKE-UP WATER
BLOWDOWN
ASH HANDLING SYSTEM
CHEMICALS
WATER
WASTE WATER
COAL PILE
RUN-OFF
FLOOR AND YARD DRAINS
WASTE WATER
REFERENCE: BU 087

Figure A-1. Sources of wastewater in a fossil-fueled steam-electric plant.

In the following discussion, each of the wastewater sources just listed will be described in terms of the potential priority pollutants which it contains. To the greatest extent possible, the composition and flow rate of the streams will be characterized. This review provides a basis for the discussions of treatment technologies presented in the Sections 4 and 5 of this report.

COOLING WATER SYSTEMS

The primary water user in utility power plants is the cooling water system. Plants employ either once-through or recirculating systems in which the cooling water is recycled and a blowdown stream is drawn off to control water quality. These systems are described below.

Once-Through Cooling Water

Once-through cooling systems are unique since the total cooling water flow is discharged as a wastewater effluent. This cooling water flow rate is approximately 0.1 liters/Kcal of heat removal for every 10 °C of cooling water temperature rise (12 gal/1000 Btu of heat removal for every 10 °F of cooling water temperature rise). After passing through the condenser, the cooling water is discharged to a receiving body (i.e., river, lake, pond).

Due to the nature of a once-through system, the chemical composition of the effluent water is essentially equivalent to that of the influent water. Water quality parameters such as total dissolved and suspended solids, pH, etc., should be largely governed by the characteristics of the cooling water source, and not by the operation of the cooling system. Slight changes in the chemical compositions between influent and effluent for these systems may occur, however, due to (1) formation of corrosion products and/or (2) addition of treatment chemicals.

Water-side corrosion of the main condenser will result in corrosion products (i.e., metal oxides) appearing in the cooling water effluent. Condenser metallurgy would normally be selected, so as to minimize water-side corrosion problems. For this reason, negligible quantities of corrosion products should appear in the effluent cooling water (EN-127).

Extensive cooling water treatment is normally precluded in once-through system due to the large quantities of raw water used. However, chemical treatment with biocides is often necessary to control the growths of algae and slime that can accumulate on condenser surfaces, retard heat transfer, and obstruct cooling water flow. Chlorine is the most common biocide used. Sodium hypochlorite is also used extensively in the utility industry.

Cooling water systems are generally chlorinated by "shock" or "slug" treatment methods. The duration of the treatment can range from five minutes to two hours, but typically lasts 30 minutes. The frequency of chlorine treatment can range from one to ten times per day (typically once per shift or three times per day) (MA-230). During chlorination, free residual chlorine is usually kept between 0.1 and 0.2 mg/ℓ (ppm) in the condenser effluent. However, when using certain influent waters, such as seawater, chlorine concentration as high as 12 mg/ℓ (ppm) or more may be used to inhibit crustacean growth (MA-230).

Cooling Tower Blowdown

Recirculating cooling systems employ cooling devices such as cooling towers, spray ponds/canals, etc., which allow the reuse of cooling water. These devices promote cooling primarily by evaporating a portion of the recirculating water flow. For this reason, dissolved, non-volatile impurities and contaminants that come into the system with makeup water are concentrated. A blowdown stream must be withdrawn from these systems to control the concentrations of impurities and contaminants. This stream represents the recirculating cooling system wastewater. Blowdown quantity is set by the maximum concentration of a limiting impurity (i.e., hardness, dissolved solids, suspended solids) that can be tolerated in the system or by the solubility limit of scaling salts such as calcium sulfate, calcium carbonate, etc. The blowdown rate typically ranges between 0.5 and 3.0% of the recirculating water flow (DO-051). The recirculating flow required is about 0.1 ℓ/Kcal of heat removal for every 10 °C of cooling water temperature rise (12 gal/1000 Btu for 10°F).

The blowdown from a recirculating cooling system will have the same chemical composition as the recirculating water. The major factors that influence cooling water composition include:

- makeup water characteristics,
- chemical treatment of the recirculating cooling water,
- intimate contacting of air-water in the cooling device, and
- cycles of concentration.

Makeup water to recirculating cooling systems replenishes water lost due to evaporation, entrainment (or drift) and blowdown. Makeup water brings soluble chemical species such as sodium (Na^+), potassium (K^+), calcium (Ca^{++}), magnesium (Mg^{++}), chloride (Cl^-), nitrate (NO_3^-), sulfate ($SO_4^=$), and carbon dioxide (HCO_3^- and $CO_3^=$) into the system. The degree of concentration of these species is governed by the operating characteristics of the cooling system, such as blowdown, drift, and evaporation rates. Soluble constituents in makeup water are concentrated to levels typically ranging from 1,500 to 10,000 mg/ℓ before being removed in the blowdown stream (MA-230). The chemical species contributing to the salinity of the blowdown is primarily determined by makeup water composition.

Chemical treatment is commonly practiced in recirculating cooling systems to control corrosion, scaling, and biological fouling. Table A-1 summarizes some of the treatment methods employed and also presents their impact on the quality of the blowdown stream.

The intimate contact which occurs between air and water in the cooling device enables particulate matter and soluble gases to be scrubbed from the air contacted. In addition, cooling towers can introduce contaminants into the air. Airborne solids captured by the cooling water can contribute significantly to the solids that accumulate in the cooling system. It is estimated that, in dusty regions, up to 80% of the suspended solids in recirculating systems originally come into the system as airborne particulates (GL-028). Upon dissolution, water soluble particulates will increase the concentrations of dissolved species in the circulating water as well. Soluble gases give rise to anionic species in the cooling water. For example, carbon dioxide (CO_2, nitrogen oxides (NO_x), sulfur oxides (SO_x) yield carbonates ($CO_3^=$ and HCO_3^-), nitrates (NO_3^-), and sulfates ($SO_4^=$) in the cooling water, respectively, when these gases are scrubbed from the air.

Leaching of preservatives from treated wood cooling towers constitutes an additional source of potentially hazardous components in cooling water blowdown. Preservatives commonly used include acid copper chromate (ACC), chromated copper arsenate (CCA), creosote and pentachlorophenol. The extent of this leaching is not currently known.

Additional potential contaminants which may be present in some cases include insecticides and herbicides from agricultural runoff, or phenolic compounds from vegetation decay, most of which are considered toxic. Chlorine addition to control biological fouling can result in chlorination of these or other hydrocarbons entering with the makeup and result in highly undesirable reaction products.

TABLE A-1. CHEMICAL TREATMENT SUMMARY FOR RECIRCULATING COOLING SYSTEMS

Treatment Objective	Chemical Additive	Typical Additive Concentrations in Blowdown	Comments	Reference
Corrosion Inhibition	Chromate	10-50 mg/ℓ as CrO_4	Chromate treatment has been the traditional corrosion inhibitor system. Since chromate has been found to be highly toxic to aquatic life, water treatment vendors are now offering alternative corrosion inhibitor treatments which employ various combinations of chromate, zinc, phosphate, silicate, and organic additives. These alternative treatments are designed to either minimize the chromate concentration that is necessary for corrosion protection or to completely eliminate the need for chromate by substituting other chemical additives.	AY-007 GL-028
	Zinc	8-35 mg/ℓ as Zn		
	Phosphate	15-60 mg/ℓ as PO_4		
	Silicates	----		
	Proprietary Organics	3-10 mg/ℓ as organic		
Scale Control	Acid Treatment	Cooling water pH is maintained between 6.5 and 8.0	Scale control allows recirculating cooling systems to operate at higher concentration factors without the formation of scale on condenser heat transfer surfaces. Acid treatment, polyphosphates, and chelating agents maintain the solubility of the common scaling salts (i.e., $CaCO_3$, $CaSO_4$, etc.) below the scaling limit (the point at which they will precipitate from solution). Polyelectrolyte antiprecipitants allow supersaturation of the cooling water with respect to scaling salts without precipitation of these salts occurring. Dispersants do not inhibit scale precipitation, but prevent precipitated salts from settling and adhering to heat transfer surfaces.	AY-007 MA-230
	Inorganic Polyphosphates	2-5 mg/ℓ		
	Chelating Agents	----		
	Polyelectrolyte Antiprecipitants	1-2 mg/ℓ		
	Organic/Polymer Dispersants	20-50 mg/ℓ		
Biological Fouling (algae, slimes, fungi) Control	Chlorine	< 0.5 mg/ℓ residual Cl_2	Biocides used to control biological fouling are either the oxidizing or non-oxidizing types. Oxidizing biocides (chlorine and hypochlorite) have been discussed for once-through cooling systems in the "Once-Through Cooling Water" section. These biocides are used in recirculating cooling systems in a fashion similar to that described for once-through systems. Non-oxidizing biocides (chlorophenates, thiocyanates, organic sulfur compounds, etc.) are employed when other chemical additives such as organic corrosion inhibitors, scale control agents, or solids control agents are destroyed by the conventional oxidizing biocides.	EN-127 AY-007 MA-230
	Hypochlorite	----		
	Chlorophenates			
	Thiocyanates			
	Organic Sulfur Compounds	< 30 mg/ℓ residual concentrations		
Suspended Solids Dispersion	Tannins	----	Chemical dispersants maintain suspended solids from settling and adhering to heat transfer surfaces.	AY-007 DO-048
	Lignins	----		
	Proprietary Organics/Polymers	20-50 mg/ℓ		
	Polyelectrolytes/Non-ionic Polymers	1-2 mg/ℓ		

BOILER OPERATIONS

The operation of the boiler involves several water streams, for steam makeup as well as for cleaning heat transfer surfaces. These systems are described below.

Boiler Blowdown

Power plant boilers are either of a once-through or drum-type design. Once-through designs are generally employed in high pressure, super-critical boilers and have no wastewater streams directly associated with their operation. However, some once-through boilers operate in the sub-critical pressure range. Drum-type boilers operate at sub-critical conditions where the steam generated is in equilibrium with liquid boiler water. Boiler water impurities are, therefore, concentrated in the liquid phase as steam is generated in these units. These impurities must ultimately be removed in a liquid blowdown stream, the wastewater from this system.

The blowdown from drum-type boilers generally contains soluble inorganic species that occur in natural waters (i.e., Na^+, K^+, Cl^-, $SO^=$, etc.); precipitated solids containing the calcium/magnesium cation; soluble and insoluble corrosion products or iron, copper, and other metals; plus a variety of chemical compounds added to the system. Dissolved solids are present in excess of all other boiler water impurities. The concentrations of impurities in drum-type boiler blowdown is largely governed by boiler operating conditions. Table A-2 presents recommended limits of total and suspended solids in drum-type boilers as a function of drum pressure.

A number of chemical additives may be present in the boiler blowdown as a result of internal boiler water treatment. Internal treatment is usually designed to control scale formation and corrosion. A summary of these internal treatment control practices is presented in Table A-3.

Scale formation is commonly inhibited by inorganic phosphate and chelating agent (EDTA and NTA) additives. Phosphates chemically combine with calcium and magnesium to form a soft sludge that is easily maintained in the fluid state. Chelating agents form soluble complexes with calcium as well as other metallic cations such as iron.

Corrosion, caused by chemical/electrochemical attack of boiler metal, can be controlled by oxygen scavenging chemical additives. Sodium sulfite and hydrazine are the oxygen scavengers most commonly employed. Their oxygen scavenging reactions are described in the following equations.

TABLE A-2. RECOMMENDED LIMITS OF TOTAL SOLIDS AND SUSPENDED SOLIDS IN BOILER WATER FOR DRUM BOILERS

	Limits Recommended for Boiler Feedwater			
Drum Pressure	Below 40 atm	40 to 68 atm	68 to 136 atm	Over 136 atm
Total solids, mg/ℓ	*	*	0.15	0.05
Total hardness as mg/ℓ $CaCO_3$	0	0	0	0
Iron, mg/ℓ	0.1	0.05	0.01	0.01
Copper, mg/ℓ	0.05	0.03	0.005	0.002
Oxygen, mg/ℓ	0.007	0.007	0.007	0.007
pH	8.0-9.5	8.0-9.5	8.5-9.5	8.5-9.5
Organic	0	0	0	0

*No value reported

Limits Recommended for Total (Dissolved and Suspended) Solids

Drum Pressure (atm)	Drum Pressure (psi)	Total Solids (mg/ℓ)
0 - 20.4	0 - 300	3500
20.41 - 30.4	301 - 450	3000
30.51 - 40.8	451 - 600	2500
40.81 - 51.0	601 - 750	2000
51.01 - 61.1	751 - 900	1500
61.11 - 68.0	901 - 1000	1250
68.01 - 102.0	1001 - 1500	1000
102.01 - 136	1501 - 2000	750
>136	>2000	15

SOURCE: BA-185

TABLE A-3. CHEMICAL ADDITIVES COMMONLY ASSOCIATED WITH INTERNAL BOILER TREATMENT

Control Objective	Candidate Chemical Additives	Residual Concentration in Boiler Water	Reference
Scale	di- and tri-sodium phosphates	3-60 mg/ℓ as PO_4	BA-185
	Ethylene diaminetetracetic acid (EDTA)	20-100 mg/ℓ	EN-127, AY-007, BL-036
	Nitrilotriacetic acid (NTA)	10-60 mg/ℓ	EN-127, AY-007, BL-036
	Alginates	up to 50-100 mg/ℓ	AY-007, BL-036
	Polyacrylates	up to 50-100 mg/ℓ	AY-007, BL-036
	Polymethacrylates	up to 50-100 mg/ℓ	AY-007, BL-036
Corrosion	Sodium sulfite and catalyzed sodium sulfite	less than 200 mg/ℓ	MA-230, BL-036
	Hydrazine	5-45 mg/ℓ	AY-007
	Morpholine	5-45 mg/ℓ	AY-007
pH	Sodium hydroxide	Added to adjust boiler water pH to the desired level, typically 8.0 - 11.0.	EN-127, AY-007, BA-185, BL-036
	Sodium carbonate		
	Ammonia		
	Morpholine		
	Hydrazine		
Solids Deposition	Starch	20-50 mg/ℓ	AY-007
	Alginates	20-50 mg/ℓ	AY-007
	Polyacrylamides	20-50 mg/ℓ	AY-007
	Polyacrylates	20-50 mg/ℓ	AY-007
	Polymethacrylates	20-50 mg/ℓ	AY-007
	Tannins	≤200 mg/ℓ	AY-007
	Lignin derivatives	≤200 mg/ℓ	AY-007

$$Na_2SO_3 + \frac{1}{2}O_2 \rightarrow Na_2SO_4$$

$$N_2H_4 + O_2 \rightarrow 2H_2O + N_2$$

Since sodium sulfite contributes to the dissolved solids of boiler water, it is used only in boilers operating below 122 atm (1800 psi) (BA-185). Hydrazine has volatile reaction products and does not contribute to the dissolved solids content of boiler water. It is used exclusively in high pressure boilers.

Boiler water pH control is also a form of corrosion protection. Alkaline compounds are added to boiler water to maintain a pH of 8.0 to 11.0. At this pH level acidic species formed in boiler water will be neutralized before acid corrosion can occur. Carbon dioxide (CO_2), the primary cause of acid corrosion, is formed upon decomposition of carbonates which are present in boiler water. pH adjustment is made with neutralizing amines such as cyclohexylamine or other alkaline additives such as caustic soda, sodium carbonate, or ammonia.

Dispersing agents are designed to inhibit solids such as precipitated scale, sludge, corrosion products, etc., from settling and adhering to boiler heat transfer surfaces. Tannin and lignin derivatives are usually used, although a number of proprietary, synthetic organic dispersants are also available.

The quantity of blowdown water from a modern, high-pressure boiler ranges from effectively zero to an upper limit of 2.0% of the stream generation rate. The blowdown rate is typically 0.1% (AY-007). Much higher blowdown rates, typically 10%, are associated with lower-pressure steam generating systems in cases where the makeup is not demineralized. Boiler blowdown may be performed in either an intermittent or continuous fashion.

Chemical Cleaning

Operational cleaning of heat transfer surfaces is designed to remove scale and corrosion products that accumulate on the boiler's water-side and the water-side of the steam condenser. The frequency at which chemical cleaning is needed varies from plant to plant. For example, the mean time between boiler chemical cleaning is approximately 36 months. However, plant data indicate extreme variations in frequency ranging from once in 7 months to once in 100 months (EN-127).

Chemical cleaning is accomplished by either soak or circulation methods. The soak method for boiler water-side cleaning involves completely filling the boiler water-side to capacity with cleaning solution. The solution remains in stagnant contact with the boiler internals until the desired degree of cleaning is achieved. The solution circulation method is similar to the soak method in every respect, except the cleaning solution is pumped or circulated through the boiler internals. For both methods, spent cleaning solutions are discharged as a waste effluent.

The active reagents in cleaning solutions are acidic or alkaline in nature depending primarily upon the deposits they are to attack. Ninety percent of all cleaning operations employ acidic formulations that attack all forms of alkaline scale (i.e., $CaCO_3$, $Mg(OH)_2$, etc.), silica scale, and corrosion deposits containing iron. In many cases, these corrosion deposits contain copper and some acid type solvents also incorporate a copper removing solvent. The majority of these formulations contain hydrochloric acid in solution strengths ranging from 5.0 to 7.5% (AY-007). Other acid solutions contain the following constituents which are present alone or in various combinations (EN-127, AY-007, BA-185, BE-162) are the following:

Inorganic Acids

Hydrochloric (HCl)
Sulfuric (H_2SO_4)
Sulfamic (NH_2SO_3H)
Phosphoric (H_3PO_4)
Hydrofluoric (HF)

Organic Acids

Citric [$HOC(CH_2CO_2H)_2CO_2H$]
Formic (HCO_2H)
Hydroxyacetic ($HOCH_2CO_2H$)

Inorganic acids are used primarily in drum-type boilers while organic acids are used on drumless, once-through boilers. Complementary additives employed with acid solutions include (1) inhibitors to decrease acid attack of bare metal surfaces, (2) wetting agents to accelerate attack on insoluble organics, and (3) complexing agents to increase removal of specific deposits such as metallic copper.

Alkaline solutions are employed (1) to provide additional attack of deposits passive to acid attack and (2) to neutralize acid residuals resulting from acid cleanings. Alkaline solutions of ammonium sulfate and carbonate are used with oxidizing agents to remove metallic copper deposits. The oxidizing agents convert metallic copper to copper oxide (CuO). The ammonium cation (NH_4^+) dissolves CuO to allow removal with the cleaning solution. Common oxidizing agents used for attacking copper deposits include bromates, chlorates, persulfates, nitrates, nitrites, or possibly caustic soda (EN-127). Chelating agents such as EDTA added to alkaline solutions facilitate removal of iron and calcium deposits. Caustic soda combined with special additives also dissolve rust as well as disperse and emulsify organic deposits (BE-162).

Alkaline rinses are also commonly used to neutralize or passivate acid residuals remaining after acid cleaning. This rinse solution generally contains caustic sodas (NaOH) or soda ash (Na_2CO_3) at approximately 1.0% solution strengths (AY-007). High pressure, once-through boilers are rinsed with ammonia or hydrazine passivating solutions. Solution strengths are 50 and 500 mg/ℓ, respectively (BA-185).

Data for three separate cleaning operations are presented in Tables A-4 through A-6. The data are for cleaning the steam-side of a high pressure, once-through boiler and a low pressure, drum boiler plus the water-side of a main condenser, respectively. Alkaline and acidic solutions are shown for both cleanings while only an acidic solution is shown for condenser cleaning.

Spent chemical cleaning solutions can have extreme pH, high dissolved solids concentrations, and significant oxygen demands (BOD and/or COD). The pH of spent solutions ranges from 1.0 to 11.0 depending on whether acidic or alkaline cleaning reagents are employed. The dissolved solids include sodium, hardness, heavy metals, chloride, bromide, and fluoride. Tables A-4 through A-6 report only iron and copper concentrations for heavy metals. However, additional metal constituents may include nickel, zinc, and aluminum. Heavy metals for combined boiler cleaning wastes follow the general concentration trend of (EN-127):

iron > copper > nickel > zinc > aluminum

The quantity of cleaning wastes varies directly with liquid holding volume of equipment to be cleaned (BA-185). For example, Tables A-4 and A-5 show spent alkaline and acid cleaning solution quantities as equal to the water-side boiler volume. Rinse solution quantities are generally one or two times this volume.

TABLE A-4. OPERATIONAL CLEANING OF A HIGH PRESSURE, ONCE-THROUGH BOILER (1)

	Stage 1	Stage 1 Rinse	Stage 2	Stage 2 Rinse
pH	11.0	9.0	2.5-3.0	6.0-7.0
Acidity, ppm total hot, as $CaCO_3$	-	-	27,000	low
Alkalinity, ppm as $CaCO_3$	90,000	9,000	-	-
NH_3, (%)	1	0.1	(2)	(2)
Fe^{++}, ppm	-	-	60,000	600
Cu	720+	75	-	-
BOD	-	-	high	high
Suspended Solids, ppm	500	5	100	5
Volume, gal	30,000	60,000	30,000	60,000
Temperature, as drained, °F	100	100	200	200

(1) The use of ammonium salts of organic acids raises this number.

(2) Capacity-20,000 gallons; solvent system Stagel, ammonium persulfate solvent; Stage 2, inhibited 3% organic acid; deposit inventory, 200 lbs copper as Cu and 1500 lbs iron as Fe_2O_3.

Source: BE-162

TABLE A-5. OPERATIONAL CLEANING OF A LOW PRESSURE, DRUM BOILER (1)

	Stage 1	Stage 1 Rinses	Stage 2	Stage 2 Rinses
pH	11.0	9.0	<1.0	7.0-9.0
Acidity, ppm total hot as $CaCO_3$	-	-	70,000	-
Alkalinity, ppm as $CaCO_3$	90,000	9,000	-	1,000
NH_3(%)	1	0.1	0.01	-
Chloride, ppm	-	-	68,000	<6,800
Fe^{++}, ppm	-	-	6,000	600
Cu, ppm	720+	75	75	-
Bromide, ppm	1,500	150	15	-
Suspended Solids, ppm	500	5	500	100
Volume, gal	30,000	60,000	30,000	60,000
Temperature, as drained,°F	150	150	150	125

(1) Capacity, 30,000 gallons; solvent system Stage 1, bromate solvent; solvent system Stage 2, inhibited 5% hydrochloric acid and copper complexing agent; deposit inventory, 200 lbs copper as Cu and 1,500 lbs iron as Fe_2O_3.

Source: BE-162

TABLE A-6. OPERATIONAL CLEANING, MAIN CONDENSER WATER-SIDE(1)

	Solvent	Rinses
pH	2.0	7.0-9.0
Acidity, hot, ppm $CaCO_3$	30,000	-
Alkalinity, ppm $CaCO_3$	-	1,000
Ca, Mg, ppm	5,000	50
Fe, ppm total	11,000	100
Cu, dissolved, ppm	1,000	50
Suspended solids, ppm	2,000+	200
Temperature, as drained, °F	140	120

---

(1) Capacity - 1000 gallons; solvent system, 10% sulfamic acid, inhibited, 1% NaCl; Rinse - Na_2CO_3 + sodium phosphates; depository inventory, 100 lbs Ca and Mg salts, 100 lbs Fe_2O_3, 10 lbs copper.

Source: BE-162

BOILER WATER TREATMENT

Ion Exchange

Ion exchange is used to provide softening and demineralization capability in power plant water treatment systems. Water softening by ion exchange can be used for condenser cooling systems, low pressure boilers, and other evaporative processes which have a water concentrating effect. Demineralization is used exclusively as a water treatment method for high pressure boilers.

Ion exchange resins are the heart of the process and they are classified as either the cationic or anionic type depending upon their ion affinity. As the exchange resins reach their ion load capacity, they are removed from service and are regenerated. Regeneration is accomplished in three distinct steps:

- Backwashing for resin bed expansion and solids removal
- Elution of ions from the resin with a regenerant solution
- Rinsing excess regenerant and eluted ions from the resin bed

All three regeneration steps contribute to wastewater generated in the ion exchange process.

Backwashing loosens and expands the resin bed and removes suspended solids that accumulate on the resin during service flow. This process is accomplished by an upward flow of water through the resin bed. The backwash flow rate is adjusted to expand the bed volume to 80-100% greater than its settled depth; this flow is maintained for a duration of 10 to 15 minutes. Flow rates of 3.4 - 4.1 $m^3/sec/m^2$ (5-6 gallons per minute per ft^2 of bed cross-sectional area) are typical (EN-127). Raw influent to the process is generally employed as backwash water. The chemical quality of the backwash water will not be significantly altered as it passes through the ion exchange bed.

After backwashing, the ion exchange resins are treated with regenerant solutions to reactivate ion exchange capability. The regenerant solutions elute ions from the ion exchange resins and replace them with species from the regenerant solution. Hydrogen cycle cation exchange resins are regenerated with acid solutions while anion exchange resins are regenerated with alkalis. The spent regenerant solutions represent the aqueous waste associated with this step of the regeneration sequence.

Spent regenerant solutions contain ions that are eluted from the ion exchange material plus the excess regenerant that is not consumed during regeneration. The eluted ions represent the chemical species that were removed from water during the service cycle of the process. For example, regeneration of a hydrogen cycle cation exchange resin will elute such species as sodium, potassium, calcium, magnesium, etc. Similarly, ions eluted from anion exchange units will include chloride, nitrate, bicarbonate, sulfate, carbonate, etc. The distribution of these species in spent regenerant solutions vary with the quality of influent water and the efficiency of the ion exchange process.

The excess regenerant required for ion elution varies with the ion exchange resins employed. Table A-7 presents a summary of ion exchange material types and the regenerant requirements of each. With the exception of sodium cycle ion exchange, excess regenerant creates an effluent of extreme pH. Spent regenerant from cation exchange units is acidic (low pH). Alkaline (high pH) regenerants are characteristic of anion exchange units.

The final step in the regeneration process is rinsing spent regenerant solution from the ion exchange bed. The rinse water quantity varies with each resin type, but it is typically 8.0 m^3 of water per m^3 of resin for cationic resins and 10 m^3 of water per m^3 of resin for anionic resins (EN-127). Rinse water quality characteristics range from those of the spent regenerant solution to those of treated water.

Evaporation

Evaporation is a demineralization process sometimes used to treat boiler feedwater whereby raw feedwater is distilled to produce a pure condensate. Feedwater impurities concentrated in the evaporator are removed as a waste blowdown stream.

Evaporator blowdown has a high dissolved solids content. The concentration of the dissolved solids varies with the level of dissolved salts in the influent water and with the degree of concentration in the evaporator. The degree of concentration which can be achieved in the evaporator is limited by the solubility limits of calcium, magnesium, and other scaling salts. Therefore, as the scaling potential of influent water increases, the allowable degree of concentration in the evaporator decreases.

For fresh water applications the blowdown quantity necessary to maintain acceptable scaling potentials ranges from 10-40% of the water charged to the process (AY-007). This corresponds to maximum TDS of approximately 3000 mg/ℓ. However, concentrations on the order of 1000-2000 mg/ℓ are more commonly observed (EN-127, AY-007). The distribution of soluble species in the blowdown is

TABLE A-7. ION EXCHANGE MATERIAL TYPES AND REGENERANT REQUIREMENT

Ion Exchange Material	Description of Operation	Regenerant Solution	Theoretical Amount
Cation Exchange Sodium Cycle	Sodium cycle ion exchange is used as a water softening process. Calcium, magnesium, and other divalent cations are exchanged for more soluble sodium cations, i.e., $2R_c\text{-Na} + Ca^{++} \rightleftarrows (R_c)_2\text{-Ca} + 2\ Na^+$. $2R_c\text{-Na} + Mg^{++} \rightleftarrows (R_c)_2\text{-Mg} + 2\ Na^+$	10% brine (NaCL) solution or some other solution with a relatively high sodium content such as sea water	—
Hydrogen Cycle Weak Acid	Weak acid ion exchange removes cations from water in quantities equivalent to the total alkalinity present in the water, i.e., $2R_c\text{-H} + Ca(HCO_3)_2 \rightleftarrows (R_c)_2\text{-Ca} + 2H_2CO_3$	H_2SO_4 or HCl solutions with acid strengths as low as 0.5%	110 -120%
Strong Acid	Strong acid ion exchange removes cations of all soluble salts in water, i.e.,	H_2SO_4 or HCl solutions with acid strengths ranging from 2.0 - 6.0%	200 - 400%
Anion Exchange Weak Base	Weak base ion exchange removes anions of all strong mineral acids (H_2SO_4, HCl, HNO_3, etc:), i.e., $2R_A\text{-OH} + H_2SO_4 \rightleftarrows (R_A)_2\text{-}SO_4 + 2HOH$	NaOH, NH_4OH, Na_2CO_3 solutions of variable strength	120 - 140%
Strong Base	Strong base ion exchange removes anions of all soluble salts in water, i.e., $R_A\text{-OH} + H_2CO_3 \rightleftarrows R_A\text{-}HCO_3 + HOH$	NaOH solutions at approximate 4.0% strength.	150 - 300%

Sources: ST-135, DE-079

ASH HANDLING

Ash, a solid byproduct of fuel oil and coal combustion, appears in a power plant boiler in two distinct forms: bottom ash and fly ash. Bottom ash must be removed from the boiler in order to maintain system operability. Fly ash is normally collected in flue gas cleaning equipment. The conveyance of both bottom ash and fly ash to their ultimate points of disposal constitutes ash handling.

Ash handling systems employ either pneumatic or hydraulic mechanisms for ash transportation. This section addresses only the hydraulic (or wet sluicing) systems. The wastewater characteristics for coal ash and oil ash sluicing systems are discussed in the subsections below.

Coal Ash Sluicing

Coal-fired generating stations require formal ash handling facilities due to the quantity of ash produced during coal combustion. The ash content of U.S. coals ranges from 6 to 20 wt.%. The average value is approximately 11 wt. % (EN-127). The distribution between bottom ash and fly ash is greatly influenced by boiler furnace design and operating mode. The ash distribution can affect the water balance for a hydraulic ash handling system. The chemical differences between fly ash and bottom ash can also affect sluicing water quality.

Bottom ash generally forms as a fused, clinker-type material and is removed by wet sluicing. Hydraulic design considerations dictate the minimum sluice water requirements as 10-18 tons per ton of bottom ash transported. In actual practice, as high as 165 tons of water per ton of bottom ash are used depending on such factors as plant design, location, and operating circumstances (AY-007). Bottom ash has excellent settling charactersistics; therefore, sluice water will be relatively free of suspended solids if adequate residence time is supplied for sedimentation. The chemical composition of sluice will change from sluice influent to sluice effluent due to the dissolution of soluble bottom ash species into water (SC-267, AS-054).

Fly ash is collected in the dry form by cyclones, fabric filters, dry electrostatic precipitators, etc., and in a water slurry by wet scrubbers, wet electrostatic precipitators, etc. Fly ash collected in either the wet or dry form is commonly sluiced to ash ponds for sedimentation of the suspended fly ash solids. Sluice water in the pond may be (1) discharged as a waste effluent, (2) recycled for additional ash sluicing, or (3) evaporated where meteorological conditions are favorable.

The minimum sluice water quantities are set by hydraulic design considerations. For fly ash, the minimum sluice water requirement ranges from 5 to 12.5 tons per ton of fly ash transported. However, as with bottom ash sluicing, the sluice water requirement may be as high as 165 tons per ton of ash (AY-007). Flows range from 1200 to 40,000 gpd/Mw, while a typical rate for coal is 10,000 gpd/Mw.

Although fly ash has somewhat poorer settling characteristics than does bottom ash, low turbidities are observed in sluice effluents if adequate retention time in the ash pond is provided. Fly ash contains a broad spectrum of soluble inorganic salts which give rise to sodium, potassium, calcium, magnesium, chlorides, sulfates, etc., in solution. The level of these dissolved solids in solution may range from a few hundred to many thousand mg/ℓ. In addition, varying concentrations of approximately 30 different elements have been detected in both bottom ash and fly ash sluice water (AS-054). Table A-8 presents ash-pond effluent analyses for a large coal-fired plant where separate bottom ash and fly ash ponds are employed.

Sluice water pH is also affected by soluble chemical species in fly ash. Fly ash from pulverized coal burning units contain alkaline species such as oxides of sodium, potassium, calcium, and magnesium (Na_2O, K_2O, CaO, and MgO). Dissolution of these salts can increase sluice water pH to levels on the order of 10.0. On the other hand, fly ash from cyclone furnaces can yield sluice water pH as low as 5.5 due to adsorption of acidic species such as SO_2, SO_3, HCl, etc., on fly ash surfaces (AS-054). The type of coal also influences sluice pH. Western coals generally produce ashes with high lime content, while eastern coal ashes contain lower levels of alkaline species and, in some cases, higher chloride levels, resulting in acidic ash pond effluents.

Oil Ash Sluicing

The ash content of fuel oil is significantly lower than that of coal. For example, the heaviest residual fuel oil is expected to have an ash content that rarely exceeds 0.2 wt. % (BA-185). Typically oil ash is on the order of 0.1 to 0.15 wt. % for residual fuels (EN-127). The quantity of ash produced in an oil-fired plant is very small, but the settling characteristics of oil ash are not as favorable as those of coal ash. A typical flow ash for sluicing oil ash is 2000 gpd/Mw.

Oil ash contains water soluble constituents that dissolve in sluicing water. These oil ash constituents are presented in Table A-9. Sodium and vanadium compounds are commonly present. Also present are oxides and salts of nickel, chromium and iron plus organometallic compounds and carbon (soot). The soot may

TABLE A-8. ASH POND EFFLUENT ANALYSES FROM A LARGE COAL-FIRED PLANT

Parameter	Flyash Pond			Bottom Ash Pond		
	Min	Ave	Max	Min	Ave	Max
Flow (gpm)	3100	6212.5	8300	4500	16152	23000
Total alkalinity (as $CaCO_3$)	-	-	-	30	85	160
Phen. alkalinity (as $CaCO_3$)	0	0	0	0	0	0
Conductivity (umhos/cm)	615	810	1125	210	322	910
Total hardness (as $CaCO_3$)	185	260.5	520	76	141.5	394
pH	3.6	4.4	6.3	4.1	7.2	7.9
Dissolved solids	141	508	820	69	167	404
Suspended solids	2	62.5	256	5	60	657
Aluminum	3.6	7.19	8.8	0.5	3.49	8.0
Ammonia (as N)	0.02	0.43	1.4	0.04	0.12	0.34
Arsenic	<0.005	0.010	0.023	0.002	0.006	0.015
Barium	0.2	0.25	0.4	<0.10	0.15	0.30
Beryllium	<0.01	0.011	0.02	<0.01	<0.01	<0.01
Cadmium	0.023	0.037	0.052	<0.001	0.0011	0.002
Calcium	94	136	180	23	40.12	67
Chloride	5	7.12	14	5	8.38	15
Chromium	0.012	0.067	0.17	<0.005	0.009	0.023
Copper	0.16	0.31	0.45	<0.01	0.065	0.14
Cyanide	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Iron	0.33	1.44	6.6	1.7	5.29	11
Lead	<0.01	0.058	0.2	<0.01	0.016	0.031
Magnesium	9.4	13.99	20	0.3	5.85	9.3
Manganese	0.29	0.48	0.63	0.07	0.16	0.26
Mercury	<0.0002	0.0003	0.0006	<0.0002	0.0007	0.0026
Nickel	0.06	1.1	0.13	0.05	<0.059	0.12
Total Phosphate (as P)	<0.01	0.021	0.06	<0.01	0.081	0.23
Selenium	<0.001	0.0019	0.004	<0.001	0.002	0.004
Silica	10	12.57	15	6.1	7.4	8.6
Silver	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Sulfate	240	357.5	440	41	48.75	80
Zinc	1.1	1.51	2.7	0.02	0.09	0.16

Units are mg/liter unless otherwise indicated

SOURCE: RI-160

TABLE A-9. INORGANIC CONSTITUENTS OF OIL-ASH

Aluminum Oxide, Al_2O_3
Aluminum Sulfate, $Al_2(SO_4)_3$
Calcium Oxide, CaO
Calcium Sulfate, $CaSO_4$
Ferric Oxide, Fe_2O_3
Ferric Sulfate, $Fe_2(SO_4)_3$
Nickel Oxide, NiO
Nickel Sulfate, $NiSO_4$
Silicon Dioxide, SiO_2
Sodium Sulfate, Na_2SO_4
Sodium Bisulfate, $NaHSO_4$
Sodium Pyrosulfate, $Na_2S_2O_7$
Sodium Ferric Sulfate, $Na_3Fe(SO_4)_3$
Vanadium Trioxide, V_2O_3
Vanadium Tetraoxide, V_2O_4
Vanadium Pentoxide, V_2O_5
Sodium Metavanadate, $Na_2O \cdot V_2O_5 (NaVO_3)$
Sodium Pyrovanadate, $2Na_2O \cdot V_2O_5$
Sodium Orthovanadate, $3Na_2O \cdot V_2O_5$
Sodium Vanadylvanadates, $Na_2O \cdot V_2O_4 \cdot V_2O_5$
$5Na_2O \cdot V_2O_4 \cdot 11V_2O_5$

Source: BA-185

constitute a source of polynuclear hydrocarbons. The sodium compounds are highly water soluble. Their dissolution will significantly contribute to the TDS of oil ash sluice water. Vanadium is a trace element that is commonly present in heavy petroleum products although some oil sources are very low in vanadium. Vanadium and other heavy elements may also appear in sluice water as the sulfate at low pH. However, the concentrations in sluice water are presently undetermined. Suspended matter will consist of siliceous and carbonaceous particles.

Fly ash recycle in oil-fired boilers has effectively allowed collection of oil ash in the furnace as bottom ash. Dry bottom ash can actually be a saleable byproduct depending upon the vanadium content of the oil burned. Collection and dry handling of oil ash can thus eliminate wastewater discharges from oil ash sluicing operations.

COAL PILE RUNOFF

Coal-fired power stations maintain reserve fuel on the plant premises in active and/or inactive coal storage piles. Active coal storage is open and is exposed to all ambient conditions. Inactive coal piles are commonly sealed with a tar spray or some other impervious covering which provides protection from the weather. Runoff from active coal storage piles is of primary concern in this section.

Precipitation runoff from active coal storage piles commonly exhibits extreme pH and contains soluble chemical species and suspended solids. The primary cause of runoff contamination is a reaction mechanism similar to the one that produces acid mine drainage. Inorganic sulfur in the coal reacts with moisture and oxygen in air to produce sulfuric acid. Also, organics may be present in the runoff.

When rainwater seeps into the coal pile, sulfuric acid is leached from the coal. The pH of the runoff effluent can be as low as 2-3 units. The acidic nature of this water drives the dissolution of inorganic salts that are present in the coal. In addition to a high sulfate anion concentration, the runoff contains high concentrations of cations such as iron, aluminum, and manganese. Cadmium, beryllium, nickel, chromium, vanadium, zinc, and copper have also been reported in trace amounts. Coal fines and other insoluble material appear in the runoff as suspended solids.

Table A-10 presents plant data for coal pile runoffs. Coal type has a great influence on runoff characteristics. For example, some coals such as are burned at Plant 5305 have sufficient alkalinity to neutralize all of the sulfuric acid formed. The resulting effluent pH in such cases ranges from 6.5 to 7.5. The higher pH range decreases the solubility of many inorganic salts, thus affecting runoff effluent quality. The runoff at Plants 1729, 3626, 0107, on the other hand, is very acidic because of the high-sulfur fuel burned. Other factors causing variations in the effluent quality besides coal type are coal pile history and runoff flow rate.

The quantity of runoff effluent is a strong function of coal pile area and local meteorological conditions. Coal pile area is primarily determined by generating station size. Power plants store from 600 to 1,800 cubic meters (0.5 to 1.5 acre-feet) of coal for each Mw of generating capacity. The storage piles are typically 8 to 12 meters (25 to 40 feet) in height (AY-007). This corresponds to a coal storage area of 50 to 225 square meters (0.013 to 0.060 acres) for each Mw of capacity, depending on pile height. An annual precipitation rate of one meter (40 inches), for example, will result in an annual runoff of between 50 and 225 cubic meters (13,000 to 60,000 gallons) per Mw of generating capacity. The typical runoff rate is 20 to 25 x 10^6 gallons per year at most coal-fired generating stations (EN-127, AY-007).

GENERAL PLANT DRAINAGE

General plant drainage refers to liquid that accumulates in floor and yard drains in the process area of a power plant as a result of precipitation runoff.

Plant drainage generally contains a high level of suspended solids consisting of such materials as soil, dust, coal fines, fly ash, etc., that are entrained in the runoff flow. Any significant degree of dissolution of these solids will also add to the dissolved salts present in the water. The specific characteristics of runoff vary radically from plant to plant and from time to time for a given plant. The general trend is that highest impurity levels are observed as initial runoff occurs. Subsequent runoff is observed to have lower impurity concentrations.

PROCESS SPILLS AND LEAKS

Liquid spills and leaks are commonly associated with overfilling of storage vessels; tank or pipe ruptures; failure of valves, pump seals, etc. Waste effluent characteristics resulting from spills and leaks depend upon the type of fluid that escapes containment. Potential fluids include:

TABLE A-10. PLANT DATA RELATING TO WATER QUALITY PARAMETERS FOR COAL PILE RUNOFF

Plant Code	3402	3401	3936	1825	1726	1729	3626	0107	5305	5305	5305
Alkalinity (mg/ℓ)	6	0	0	-	82	-	-	0	21.36	14.32	36.41
BOD (mg/ℓ)	0	0	10	-	3	-	-	-	-	-	-
COD (mg/ℓ)	1080	1080	806	85	1099	-	-	-	-	-	-
TS	1330	1330	9999	6000	3549	-	-	45000	-	-	-
TDS	720	720	7743	5800	247	-	28970	44050	-	-	-
TSS	610	610	22	200	3302	-	100	950	-	-	-
Ammonia	0	0	1.77	1.35	0.35	-	-	-	-	-	-
Nitrate	0.3	0.3	1.9	1.8	2.25	-	-	-	-	-	-
Phosphorous	-	-	1.2	-	0.23	-	-	-	-	-	-
Turbidity	505	505	-	-	-	-	-	-	8.37	2.77	6.13
Acidity	-	-	-	-	-	-	21700	27810	8.68	10.25	8.84
Total Hardness	130	130	1109	1850	-	-	-	-	-	-	-
Sulfate	525	525	5731	861	133	6837	19000	21920	-	-	-
Chloride	3.6	3.6	481	-	23	-	-	-	-	-	-
Aluminim	-	-	-	-	-	-	1200	625	-	-	-
Chromium	0	0	0.37	0.05	-	-	15.7	0.3	-	-	-
Copper (mg/ℓ)	1.6	1.6	-	-	-	-	1.8	3.4	-	-	-
Iron (mg/ℓ)	0.168	0.168	-	0.06	-	0.368	4700	93000	1.0	1.05	0.9
Magnesium (mg/ℓ)	-		89	174	-	-	-	-	-	-	-
Zinc (mg/ℓ)	1.6	1.6	2.43	0.0006	0.08	-	12.5	23	-	-	-
Sodium (mg/ℓ)	1260	1260	160	-	-	-	-		-	-	-
pH	2.8	2.8	3	4.4	7.8	2.7	2.1	2.8	6.7	6.6	6.6

Source: EN-127

- acid, alkalis, and brine solutions for ion exchange regenerants as well as other water treating chemicals
- fuel oil, transformer oil, and circuit breaker oil
- water used in plant operation such as cooling water.

MISCELLANEOUS OPERATIONS

Several miscellaneous sources of wastewater at power plants are listed below:

- laboratory and sampling operations
- auxiliary cooling system(s)
- water intake screen washings
- other

Although the impact of wastewater from these miscellaneous operations is less significant than those discussed in previous sections, these sources nevertheless contribute to the total wastewater problem.

Quantitative data which characterize wastewater from these miscellaneous sources is limited. The only data available are for auxiliary cooling systems, which remove heat from mechanical equipment items such as those listed below:

- bearing and/or gland cooling for pumps, fans, and other rotary equipment
- air compressor water jackets
- generator cooling

Auxiliary cooling systems can be either the once-through or closed-cycle types.

Once-through auxiliary cooling systems do not usually involve chemical treatment, with the exception of chlorination. Thus, water quality of the waste is determined by the influent water to the system. During chlorination of these systems, residual chlorine levels in the effluent are approximately the same as presented for condenser cooling systems as presented earlier in the sections entitled Once-Through Cooling Water and Cooling Tower Blowdown. However, the frequency of chlorination is considerably reduced.

The flow through the once-through auxiliary cooling circuit ranges from 0.0019 to 0.133 m^3/min (0.5 to 35 gpm) per Mw of rated generating capacity. The typical flow is approximately 0.040 m^3/min (10 to 11 gpm)(AY-007). This total flow represents the wastewater stream for once-through auxiliary cooling.

Wastewater from a closed-cycle auxiliary cooling system is a blowdown stream. Water in the closed cooling circuit is treated to control corrosion with inhibitors such as chromates (at levels up to 250 mg/ℓ) and borates or nitrates (at levels ranging from 500 to 2000 mg/ℓ). Water pH is maintained between 9.5 and 10 by addition of caustic soda or soda ash (AY-007). Alternatively, some plants use stream condensate ammonia and hydrazone in this cooling circuit (EN-127). The water recirculation rate is typically 0.091 to 0.095 m^3/min (23-25 gpm) per Mw of rated generating capacity. Blowdown rates vary from zero to 0.0019 m^3/day (0-5 gpd) (EN-127, AY-007).

APPENDIX B

PRELIMINARY SURVEY OF TECHNOLOGIES FOR THE CONTROL OF PRIORITY POLLUTANTS IN UTILITY EFFLUENTS

This appendix presents the results of the preliminary survey to select technologies for the control of priority pollutants in the utility industry. The controls were screened to select the technoloigies that are applicable to the utility industry.

Each technology examined is presented in this appendix. The technologies that were eliminated from further consideration are presented in Table B-1 along with the reasons for elimination. The selected control technologies are presented in detail in Section 5.

TABLE B-1. CONTROL TECHNOLOGIES ELIMINATED FROM FURTHER EVALUATION

Technology	Commercially Unproven Technology	Not Effective for Toxic Compounds*	Produces Toxic Secondary Pollution	Applicable only to Specific Toxics	Other Considerations
Activated Sludge		✓			
Aerated Sludge		✓			
Air Oxidation		✓			
Alum Precipitation and Carbon Adsorption					Similar to lime precipitation.
Barium Salt Precipitation			✓	✓	
Complex Formation and Carbon Adsorption			✓	✓	
Chemical Oxidation			✓		
Coprecipitation					This mechanism is considered in lime precipitation.
Deep Well Disposal					Not applicable to all situations.
Electrodialysis					Reverse osmosis is very similar to electrodialysis with regard to cost application. Also, reverse osmosis is more widely used by the utility industry; therefore, only reverse osmosis was considered.
Electrolytic Oxidation	✓				
Electrolytic Reduction				✓	
Ferric Chloride Precipitation and Carbon Adsorption					Similar to lime precipitation.
Foam Fractionation	✓	✓		✓	
High Density Sludge and Neutralization					Similar to lime precipitation.
Ion Exchange			✓	✓	
Liquid Waste Incineration			✓	✓	Already in use at some locations.
Chemical Reduction			✓	✓	
Photochemical Oxidation	✓				
Skimming and Flotation		✓			Already in use at some locations.
Solvent Extraction	✓		✓		
Sulfide Precipitation			✓		Similar to lime precipitation.
Ultrafiltration			✓		
Ultrasonic Oxidation	✓				
Zero Discharge					It is a strategy and not a control technology.

*The evaluation of the effectiveness of the control technologies is based upon the low concentrations anticipated in the utility industry.

ACTIVATED CARBON ADSORPTION

State of Development - Adsorption is currently being used in varied industrial applications. Several companies market carbon adsorption processes commercially.

Applications to Date -

- General - Used to remove dissolved organics from waste streams regardless of their origin.
- Specific - Applied to upgrading various waste streams in the following industries:
    - Detergent manufacturing in New Jersey (removal of xylene, alcohols, TOC from effluent wastewater)
    - Oil refining in California and Pennsylvania (removal of COD from effluent wastewater)
    - Chemicals manufacturing in Alabama (removal of phenols, resin intermediates from wastewater)
    - Resin manufacturing in New York (removal of xylene, phenols from effluent wastewater)
    - Herbicide manufacturing in Oregon (removal of toxic phenols from wastewater)
    - Coking plants in Pennsylvania (removal of phenols from ammonical liquor)

Process Description - Activated carbon adsorption can be used to remove a variety of organic and some inorganic toxic contaminants from industrial wastewaters. When the carbon becomes saturated, it is regenerated and returned to service. Carbon losses during regeneration are usually 5-10% of the original volume.

Expected Performance - Carbon adsorption has exhibited the following removal efficiencies in various applications (Table B-2).

TABLE B-2. CARBON ADSORPTION REMOVAL EFFICIENCIES

Contaminant	% Removal Efficiency	Reference
Acrolein	30.6	GI-121
Arsenic (and compounds)	13.0	ES-020
Chlorinated Benzenes	Some removal expected	MI-265
Chlorinated Phenols	Some removal expected	MI-265
Cyanides	1.0	VA-127
Mercury	30.0	ES-020
Nickel	32.0	ES-020
Pentachlorophenol	Some removal expected	MI-265
Phenol	99	VA-127
Zinc	6.0	ES-020
Benzene	95.0	GI-121
Toluene	79.2	GI-121
2,4 Dichlorophenol	Some removal expected	GI-121
Chromium	Some removal expected	GI-121
Copper	15	GI-121
Cadium	0	ES-020
Selenium	50	ES-020
Lead	Some removal expected	ES-020

Costs - Capital costs

- Capital cost (Replacement cost not installed cost) vs. design capacity (1968 dollars).

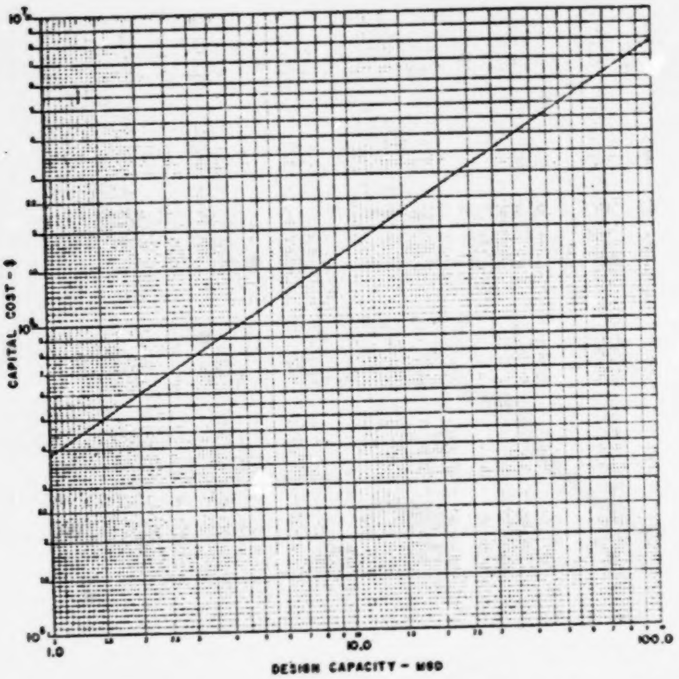


Figure B-1. Carbon adsorption capital cost relationship.

Source: DA-052

- Herbicide manufacturing installed capital cost (1971 dollars) (Table B-3).

TABLE B-3. CARBON ADSORPTION CAPITAL COSTS

Activated carbon system	
2 Adsorber vessels (wooden)	$ 13,300
2 Carbon storage vessels	10,400
Recycle water vessel	3,500
Quench tank	500
Pumps and eductors	5,900
Reactivation furnace*	35,400
Afterburner and stack	6,300
Stack gas scrubber	10,000
Dewatering screw	6,900
Piping and misc. material	26,500
Electrical	11,000
Instruments	5,800
Structures and foundations	22,800
Carbon inventory	18,500
Construction labor	31,400
Engineering	21,800
Subtotal	$230,000
Neutralization system	40,000
Water collection system	30,000
Total	$300,000

*Excluding installation

Source: HE-188

Operating Costs

- Coke plant waste effluent (1972 dollars)
(Figures B-2 and B-3 are on next page)

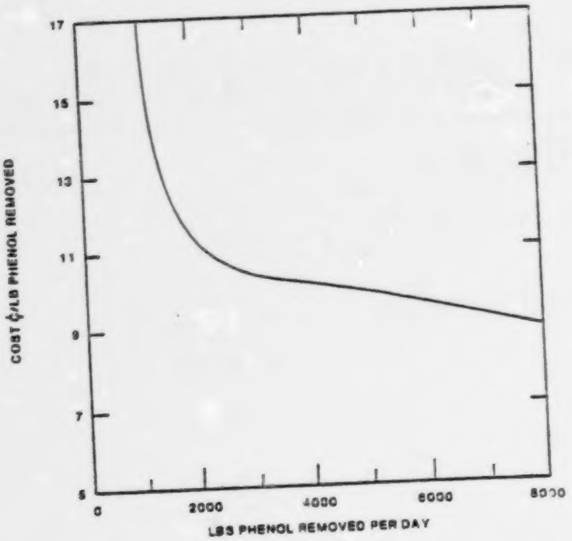
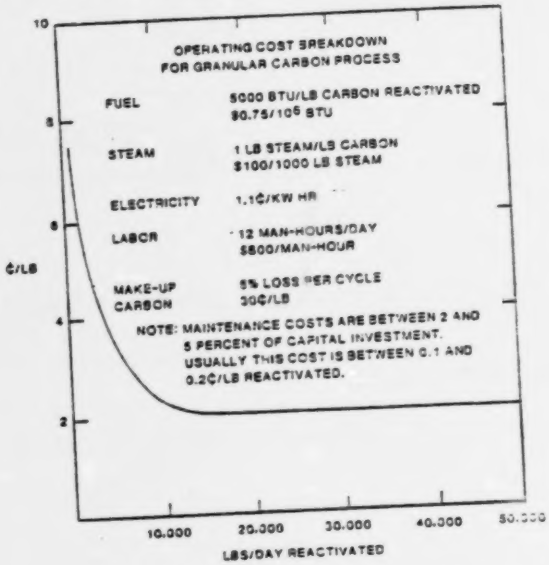


Figure B-2. Cost of phenol removal by activated carbon.



OPERATING COST BREAKDOWN
FOR GRANULAR CARBON PROCESS

FUEL	5000 BTU/LB CARBON REACTIVATED $0.75/$10^6$ BTU
STEAM	1 LB STEAM/LB CARBON $100/1000 LB STEAM
ELECTRICITY	1.1¢/KW HR
LABOR	12 MAN-HOURS/DAY $800/MAN-HOUR
MAKE-UP CARBON	5% LOSS PER CYCLE 30¢/LB

NOTE: MAINTENANCE COSTS ARE BETWEEN 2 AND 5 PERCENT OF CAPITAL INVESTMENT. USUALLY THIS COST IS BETWEEN 0.1 AND 0.2¢/LB REACTIVATED.

Figure B-3. Carbon adsorption reactivation costs.

Source: VA-127

- Water treating plant (1971 dollars)

TABLE B-4. CARBON ADSORPTION PROCESS;
ESTIMATE-10 MILLION GAL/DAY PLANT

Amortization of Capital		$/10^6 Gallons
$1,860,000; 20 years @ 5%		$41.00
Operation and Maintenance		
Power	$ 8.50	
Labor	18.00	
Maintenance Materials	5.00	
Carbon Regeneration		
Power, Gas and Water	2.50	
Makeup Carbon (10% Loss)	11.00	
		45.00
		TOTAL = $86.00

Source: EM-019

Other Process Emissions - Activated carbon adsorption does not generate any polluted effluents. However, the regeneration process generates a stream containing suspended solids and potentially contaminated flue gas.

References - ES-020, GI-121, MI-265, VA-127, DA-052, HE-188, EM-019.

ACTIVATED SLUDGE

State of Development - In commercial use.

Applications to Date - Numerous petroleum refineries in the U.S. use this process currently. It is used as an end-of-pipe treatment system for removing colloidal solids and carbonaceous wastes. Thus, it primarily controls organic compounds and suspended solids.

Process Description - Activated sludge procedures are used extensively for coagulating and removing nonsettleable colloidal solids, as well as to stabilize organic matter. EPA reports (8) removal efficiencies of 80-99% for BOD, 50-95% for COD, 60-85% for suspended solids, 80-99% for oil, 95-99+% for phenol, 33-99% for ammonia, and 97-100% for sulfides. Thus, a high quality effluent is obtainable from a properly designed and operated activated sludge system.

This particular process is an aerobic biological procedure containing, within a reaction tank, a high concentration of microorganisms, which is maintained by recycling activated sludge. Oxygen is supplied to the wastewater in the reaction tank either by mechanical aerators or a diffused-air system. Inasmuch as the microorganisms remove the organic materials by biochemical synthesis and oxidation reactions, the converted organic matter must be removed by sedimentation, prior to final discharge.

The main components of the process are the aeration, or reaction vessel and the sedimentation tank. Sludge removed from the sedimentation tank is recycled to the aeration vessel to maintain the required concentration of microorganisms. Since a portion of the sludge must be discarded, it is first dewatered and then used as landfill.

Expected Performance - EPA reports removal efficiencies of 80-99% for BOD, 50-95% for COD, 60-85% for suspended solids, 95-99% for phenol, 33-99% for ammonia, and 97-100% for sulfides. Within the electric utility industry it has potential for removing organics and trace metals. Therefore, it could be used for controlling toxic pollutants in every utility effluent stream.

Costs - The following costs were obtained from EN-487, p. 129-131. Initial investment: \$.097/gpd[1]; \$0.75/gpd[2]; \$0.65/gpd[3].

Annual Costs -	Case 1	2	3
Capital (10%)	\$0.097	0.075	0.065
Dep. (20%)	0.194	0.150	0.130
Operating	0.078	0.065	0.057
Energy (40% Oper. Cost)	0.031	0.026	0.023
	\$0.400/gpd	\$0.316/gpd	\$0.275/gpd

[1] 3.12 x 10^6 gals/day wastewater flow

[2] 7.6 x 10^6 gals/day wastewater flow

[3] 15.6 x 10^6 gals/day wastewater flow

Other Process Emissions - Activated sludge systems result in a solid waste discharge. The sludge which is discharged is first dewatered and then used as landfill. Incineration offers an improved method of disposal of the sludge, but its application is is not widespread.

References - EN-407, BU-215, TE-111, BE-156.

AERATED LAGOONS

State of Development - In commercial use.

Applications to Date - Numerous petroleum refineries in the U.S. use this process currently.

Process Description - Aerated lagoons operate generally by the same basic principles as do oxidation ponds. Mechanical-aeration equipment, associated with aerated lagoons, results in a higher concentration of bacteria than is present in oxidation ponds. Consequently, land requirements are less for aerated lagoons than for oxidation ponds having equal loadings. Retention time is usually 3-10 d. Removal efficiencies are 75-95% for BOD, 60-85% for COD, 40-65% for suspended solids, 70-90% for oil, 90-99% for phenol, and 95-100% for sulfides.

Aeration of the lagoon keeps most of the solids in suspension. One method of decreasing the suspended solids in the effluent is to have a sedimentation section in the lagoon, where the water is calm enough and the residence time is adequate to allow sedimentation of the solids. Otherwise, it may be necessary to include a settling tank.

Since, like the oxidation pond, an aerated lagoon is sensitive to temperature, in colder climates the performance is hampered during the winter months. Some sources recommend that solids be returned to the lagoon during the winter to improve performance, so as to operate the lagoon essentially the same as the activated sludge process. In a development program, it is very convenient for the aerated lagoon to be the first step, so that simply by adding clarifiers, sludge-return pumps, and additional aeration equipment, the lagoon becomes an activated sludge system.

Expected Performance - Reported removal efficiencies for aerated lagoons is 75-79% for BOD, 60-85% for COD, 40-65% for suspended solids, 70-90% for oil, 90-99% for phenol, and 95-100% for sulfides.

Costs - Capital cost - $0.20/1000 gpd of wastewater flow.

Other Process Emissions - Aerated lagoons result in a solid waste discharge of sludge. The sludge is usually dewatered and then landfilled or incinerated for disposal.

References - EN-407, BU-215, KI-072, BE-156, BE-012, BA-185.

AIR OXIDATION

State of Development - Commercially available

Applications to Date - This technique is applied in various industries.

Process Description - Air is the least expensive and, therefore, potentially the most desirable oxidizing agent. Phenols are slowly oxidized by bubbling air through their aqueous solutions. Indeed, 70-80% of the phenols in normal sewage may be removed by vigorous aeration with compressed air for 1-2 hours. The phenols are thus oxidized to slightly soluble polymers which can be removed by filtration. The oxidation of phenols by this method is favored in the presence of suspended matter, particularly lime. Industrial phenolic wastes may be aerated in the presence of powdered coal or iron- or magnesium-containing slag or ash. These materials appear to exert a catalytic effect on the air oxidation reaction and, after several hours, the phenol concentration will be reduced by 80-85%. The initial oxidation products are believed to react with the monophenols to produce insoluble materials which are adsorbed by the slag. Soil or wood charcoal may be used in a similar manner.

In a process described recently, phenolic wastes, at pH 7-11 and 60-70°, are sprayed into the top of a cooling tower and recycled for a total residence time of 16 hours. Monobasic phenols are completely oxidized to aliphatic acids and carbon dioxide. It is not clear whether this system operates by the direct oxidation of the phenols by air or is, in fact, an example of biological oxidation using the "oxidation tower" process.

Expected Performance - Air oxidation has exhibited the ability to remove 80-85% of the phenols in the wastewater.

Cost - The treating costs associated with attaining 80-85% phenol removal are $.01/lb phenol (not including pretreatment costs).

Other Process Emissions - This process does not generate any contaminated streams.

References - EI-026

ALUM PRECIPITATION AND ACTIVATED CARBON ADSORPTION

State of Development - All the unit processes in this control scheme are commercially available.

Process Description - This control scheme consists of: 1) chemical addition, 2) settling, 3) filtration, and 4) carbon adsorption. The primary function of this scheme is to remove heavy metals from a waste effluent.

Application to Date - This control scheme was investigated by the Wastewater Research Division of EPA at Cincinnati, Ohio, and is being proposed for application to several types of wastewaters.

Expected Performance - Highly concentration dependent

TABLE B-5. REMOVAL EFFICIENCIES FOR ALUM PRECIPITATION AND ACTIVATED CARBON ADSORPTION

		Concentration	
Contaminant	% Removal Efficiency	In (mg/ℓ)	Out (µg/ℓ)
Chlorinated benzenes	Some removal expected		
Chlorinated phenols	Some removal expected		
Cyanides	Some removal expected		
Mercury	98.3	0.06	1.0
Nickel	37.0	0.9	567.0
Zn	28		
Cr	97		
Cu	98		
Sb	71		
Be	99		
Cd	56		
Pb	97		
Se	56		
Ag	99		
Th	39		
Pentachlorophenol	Some removal expected		
Phenol	Some removal expected		
Benzene	Some removal expected		
Toluene	Some removal expected		
2,4-Dichlorophenol	Some removal expected		

BARIUM SALT PRECIPITATION

State of Development - In commercial use

Applications to Date - Specialized applications such as electroplating wastes.

Process Description - Hexavalent chromium can be removed from waste waters by precipitation as a barium salt. Barium chloride is added in strictly controlled amounts to effect the formation of insoluble barium chromate according to the reaction:

$$BaCl_2 + Na_2CrO_4 \rightarrow BaCrO_4 + 2NaCl$$

The major disadvantages of these processes are that a toxic sludge is produced and that the $BaCl_2$ must be carefully controlled as it is a highly toxic chemical.

Expected Performance - The solubility of barium chromate is given as 4.4×10^{-4} grams per 100 cc at 28°C. Thus, a residual concentration of about 1 ppm Cr^{+6} would be expected due to the solubility of $BaCrO_4$.

Costs - No data available

Other Process Emissions - A toxic barium chromate sludge

References - SM-519

CHEMICAL OXIDATION

State of Development - In commercial use

Applications to Date - A number of the waste components resulting from mining, milling, and electroplating may be removed or rendered less harmful by oxidation. Among these are cyanide, sulfide, ammonia, and a variety of materials presenting high COD levels.

Process Description - Alkaline chlorination of rinse waters completely decomposes cyanide at room temperature. The cyanide radical is converted to carbonate and nitrogen gas according to the following reaction:

$$2NaCN + 5Cl_2 + 12NaOH \rightarrow N_2 + Na_2CO_3 + 10NaCl + 6H_2O$$

The use of caustic to produce high or alkaline pH also results in the precipitation of heavy metal hydroxides. Cyanide can also be destroyed using hypochlorites.

Cyanide is converted to cyanite, CNO, as an intermediate step in complete oxidation. Among the other oxidants used to convert cyanide to cyanate is hydrogen peroxide which has been used in Europe for treating cyanide waste streams from metal finishing plants. Ammonia may also be removed through oxidation by ozonation.

Expected Performance - Chemical oxidation can remove cyanides and phenols to very low residual levels. Chlorine, ozone, and chlorine dioxide are all capable of removing cyanides and phenols to below 0.003 mg/ℓ residual concentration. Chemical oxidation could potentially be applied to the control of cyanides or phenols in the following utility plant streams: cooling tower blowdown, metal cleaning wastes, ash pond overflow, coal pile runoff, and yard drainage.

Costs - Direct chemical costs for alkaline chlorination of cyanide are given as $1.93/lb of CN based on chlorine to cyanide ratio of 10:1 and caustic to cyanide ratio of 6:1. Liquid chlorine is valued at 11.5¢/lb and liquid 50% caustic at 13¢/lb.

Energy Requirements - Ozonation is the only chemical oxidation technique which requires significant energy input. This requirement is approximately 23.15 kW-hrs per kilogram of ozone produced. This is equivalent to about 20 kW-hrs/day for treating a 100 gpm stream containing a cyanide/phenol total concentration of 1 mg/ℓ.

Other Process Emissions - The use of alkaline chlorination nearly always results in sludge formation. The sludge is composed of the precipitated metal hydroxides and, if lime is used to provide alkalinity, it also contains calcium carbonate and possibly calcium sulfate.

References - EN-394, HO-293, RE-165, WI-260, HA-603

COMPLEX FORMATION AND CARBON ADSORPTION

State of Development - In commercial use.

Applications to Date - Removal of cyanide from electroplating rinse waters.

Process Description - The addition of ferrous sulfate to cyanide solutions produces less toxic complexes which precipitate as sludge. The process produces highly colored solutions and dark blue sludge. The process is inexpensive where cheap ferrous sulfate is available. Residual uncomplexed cyanide may be as high as 5-10 ppm and ferrocyanides in receiving streams may be decomposed by sunlight to again form cyanides. Polysulfides can also be used to form nontoxic sulfocyanates.

Copper sulfate can also be used to complex cyanide at a pH of 10. In combination with an activated carbon adsorption column, removal of 99+% of cyanide and all of the copper can be achieved.

Expected Performance - The formation of ferrocyanides results in residual cyanide levels of 5-10 ppm and possible regeneration of cyanide by sunlight decomposition. With carbon adsorption cyanide and iron levels less than 1 ppm are obtainable.

Costs - For ferrocyanide formation costs are relatively low if cheap ferrous sulfate is available. With carbon sorption, operating costs range from $0.16-0.87 per lb. of cyanide treated.

Other Process Emissions - Copper and ferrous cyanide sludges.

References - RE-165

COPRECIPITATION

State of Development - In commercial use.

Applications to Date - Coprecipitation has been used in the uranium and ferroalloy industries for control of radium and molybdenum.

Process Description - In this process materials are precipitated indirectly by combining them into particles of another precipitate. Radium in solution is controlled by the addition of barium chloride in the presence of excess sulfate, for example, down to a level of about 1 picogram per liter.

Molybdenum may also be removed from mine and mill effluents by coprecipitation with ferric hydroxide. The formation of ferric hydroxide is optimum at pH 4.5 and thus the typically alkaline mill waste streams must be acidified before coprecipitation is effected. A base is then added to neutralize the effluent prior to discharge.

Expected Performance - Method requires more study before performance level in other system could be specified.

Costs - No data available.

Other Process Emissions - Sludge

References - EN-394

DEEP WELL DISPOSAL

State of Development - In commercial use.

Application to Date - Oil field brines and chemical wastes.

Process Description - Disposal of wastes, especially oil field brines and chemical wastes, in deep wells is becoming increasingly popular as restrictions on discharging wastes to navigable waters become tighter. Such wells can be costly, especially when several are needed and depths are one or two thousand meters. as sometimes is required. Geologic conditions must be suitable, and in many parts of the country, deep wells are not practical. Sand strata at depth, especially those already naturally saline, are among the most suitable candidates for deep well disposal.

Expected Performance - Technique not commonly used but could have application in the disposal of effluents from blowdown, chemical cleaning, floor and yard drainage, plant laboratory, water treatment, coal ash handling, and coal pile drainage.

Costs - Extremely variable dependent primarily on geologic conditions.

Other Process Emissions - Potential secondary pollution of underground water.

References - EN-392, EN-127.

ELECTRODIALYSIS

State of Development - Commercially available.

Application to Date - Desalination of water.

Process Description - Under the influence of an electric field the ionic species are transferred through ionic membranes leaving a desalinated water. Some water pretreatment may be required.

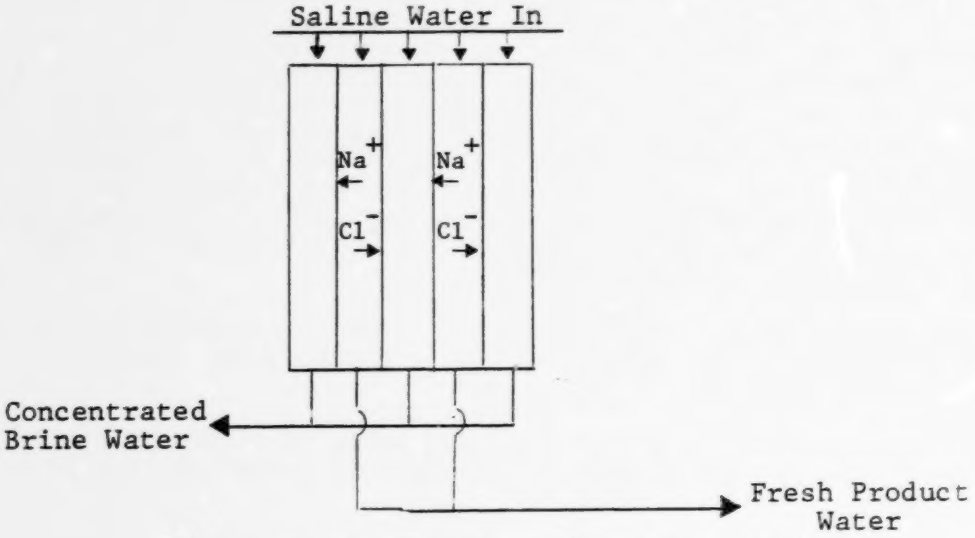

Saline Water In
Na^+
Na^+
Cl^-
Cl^-
Concentrated Brine Water
Fresh Product Water

Figure B-4. Flowsheet for electrodialysis.

Expected Performance - 60-95% TDS removal

Costs - Operating costs 40¢-50%/1000 gal of water processed

Energy Requirements - 7-15 kW-hr/1000 gal of water processed

Other Process Emissions - Concentrated brine

References - EN-394, RI-160, Vendor contract (Ionics, Inc., Watertown, Massachusetts).

ELECTROLYTIC OXIDATION

State of Development - Exists on a laboratory scale, however, no industrial applications cited.

Applications to Date - No industrial applications cited.

Process Description - An electrolyte, such as sodium chloride, is added to the wastewater, and, using an anode of platinum, lead oxide or carbon and an iron or stainless steel cathode, a potential of 3-4 volts is applied at a current density of 0.5-0.8 amps/sq. in. Phenol concentrations as high as several g/ℓ may be effectively reduced with a power consumption of 0.3-0.5 kW-h/g of phenol. During electrolysis, the oxygen formed at the anode oxidatively degrades the phenol at a rate proportional to the current density and inversely proportional to the phenol concentration. During the oxidation reaction, phenols are converted to polyhydroxy benzenes, quinones, and by ring cleavage, to oxalic and formic acids. Only 6-17% of the phenol is completely oxidized to carbon dioxide.

Expected Performance - For an initial phenol concentration of 2000 ppm, electrolytic oxidation has achieved a 95% removal efficiency of phenols.

Costs - For an initial phenol concentration of 2000 ppm and a 95% phenol removal efficiency, the treating costs of electrolytic oxidation are $1.53-$3.06/lb. phenol.

Other Process Emissions - None

References - EI-026

ELECTROLYTIC REDUCTION

State of Development - In commercial use.

Applications to Date - Electrolytic reduction is currently being used for the treatment of cooling tower blowdown for chromate and zinc removal in the chemical processing industry. It is also being applied for silver recovery from photographic industry wastewaters.

Process Description - The electrolytic reduction process uses iron anodes and cathodes to remove chrome from cooling tower blowdown. Basically, chromate is removed from the blowdown stream according to the following reaction:

$$Cr_2O_7^{-2} + 6Fe(OH)_2 + 7H_2O \rightarrow 2Cr(OH)_3 + 6Fe(OH_3) + 2OH^-$$

The ferrous hydroxide is formed at the cathode. The completed reaction is followed by the subsequent precipitation of ferric hydroxide and chromic hydroxide as a complex.

Operationally, the cooling tower blowdown enters an electrochemical cell near the top of its outer jacket. The wastewater flows down through the jacket to the cell bottom and then up through the center compartment. Here it contacts the electrodes where the chromate is reduced and then overflows from the cell top. The pH range of the water must remain between 6 and 9 for proper operation.

Following reduction, the chromium hydroxide precipitate must be removed. This may be accomplished by a number of methods including lagooning, clarification, or filtration.

Operation of this electrochemical process is continuous except for the short-term shutdowns required for replacement of electrodes and daily acid washes. Electrodes must be replaced every two to three weeks.

Expected Performance - Electrolytic reduction is potentially capable of removing chromium and zinc in cooling tower blowdown from power plants. Chromium can be consistently removed to below 0.05 ppm and zinc can be removed to 0.10 ppm (DI-150).

Costs - The installed capital cost for an electrolytic reduction system for chromate removal to 0.05 mg/ℓ residual for a 500 gpm flow rate is about $500,000. The operation and maintenance costs run about $0.55 per 1000 gallons treated.

Energy Requirements - The power requirements for electrolytic reduction generally run below 5 kW-hrs per pound of hexavalent chrome removed. This is equivalent to about 0.36 kW-hrs of energy per 1000 gallons of water treated (DI-150). This energy is primarily that used for the electric current to the electrodes.

Other Process Emissions - The chromium hydroxide and iron hydroxide precipitates constitute a secondary process emissions from electrolytic reduction. The precipitate must be treated for removal by a clarification step prior to discharge.

References - DI-150, PA-120.

EVAPORATION POND

State of Development - In commercial use.

Applications to Date - In present practice, many of the mining and milling operations in the western and southwestern United States employ solar evaporation as a principal means of water treatment. Similarly, some utilities as well as other industries rely on solar ponds in water management.

Process Description - The solar evaporation of water from a solution to leave a solid residue is a low cost treatment technique. Except for solar energy as a means for evaporation, this method has limited applications. Energy requirements are very high for non-solar methods and the residues are water soluble materials which may present a disposal problem.

Expected Performance - Evaporative losses of water at some installations may exceed 7,572 cubic meters (2,000,000 gallons) per year for each 0.4 hectare (1 acre) of evaporative surface; with adequate surface acreage, this loss may allow for zero-effluent-discharge operation.

Costs - Costs are low, and energy demands are virtually nil. Land availability and cost of excavation are major factors in the applicability of evaporation ponds.

Other Process Emissions - Volatile toxics in effluent streams may result in secondary air emissions.

References - EN-392, EN-394.

FERRIC CHLORIDE PRECIPITATION AND ACTIVATED CARBON

State of Development - All the unit processes in this control scheme are commercially available.

Application to Date - This control scheme was investigated by the Wastewater Research Division of EPA at Cincinnati, Ohio, and is being proposed for application to several types of wastewaters.

Process Description - This control scheme consists of: 1) chemical addition, 2) settling, 3) filtration, and 4) carbon adsorption. The primary function of this scheme is to remove heavy metals from a waste effluent.

Expected Performance - Highly concentration dependent.

TABLE B-6. REMOVAL EFFICIENCIES FOR CHLORIDE PRECIPITATION AND ACTIVATED CARBON

		Concentration	
Contaminant	% Removal Efficiency	In (mg/ℓ)	Out (μg/ℓ)
Chlorinated benzenes	Some removal expected		
Chlorinated phenols	Some removal expected		
Cyanides	98.	.05	
Mercury	99.	.05	1.0
Nickel	37.0	5.0	3150.
Pentachlorophenol	Some removal expected		
Phenol	Some removal expected		
Benzene	Some removal expected		
Toluene	Some removal expected		
2,4-Dichlorophenol	Some removal expected		
Zinc	94.	5.0	330.
Chromium	99.3	5.0	35.
Copper	96.0	5.0	36.
Antimony	72.0	.5	140.
Beryllium	98.9	.1	1.
Cadmium	98.6	5.0	70.
Lead	98.1	5.0	45.
Selenium	80.0	.1	20.
	75.0	.05	13.
Silver	99.1	.5	5.
Thallium	45.0	.6	330.
Arsenic	97.1	5.0	140.

Costs -

Chemical Costs (1976 dollars)

- Ferric chloride - \$5 per 100 pounds (Ref. March 21, 1977, Chem. Mark. Report.)

Settler Costs (1968 dollars) - not installed

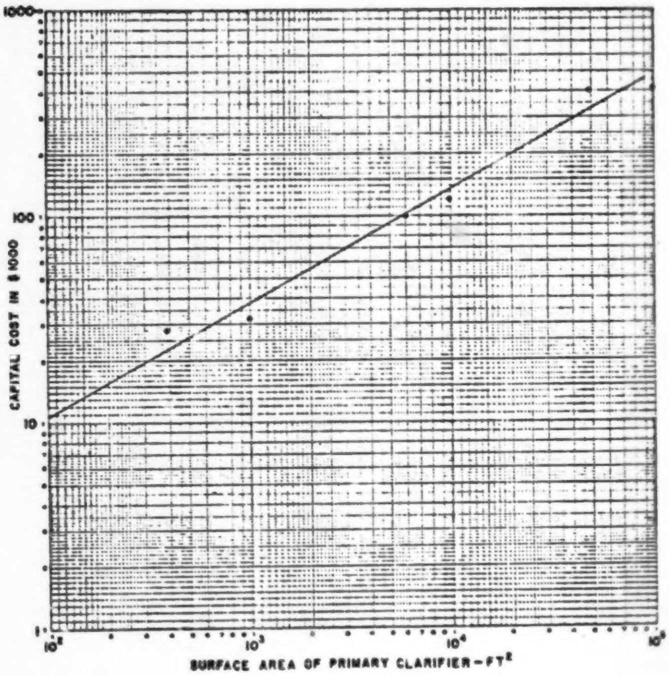


Figure B-5. Primary sedimentation capital cost relationship.

Source: DA-052

Filtration Costs (1968 dollars) - not installed

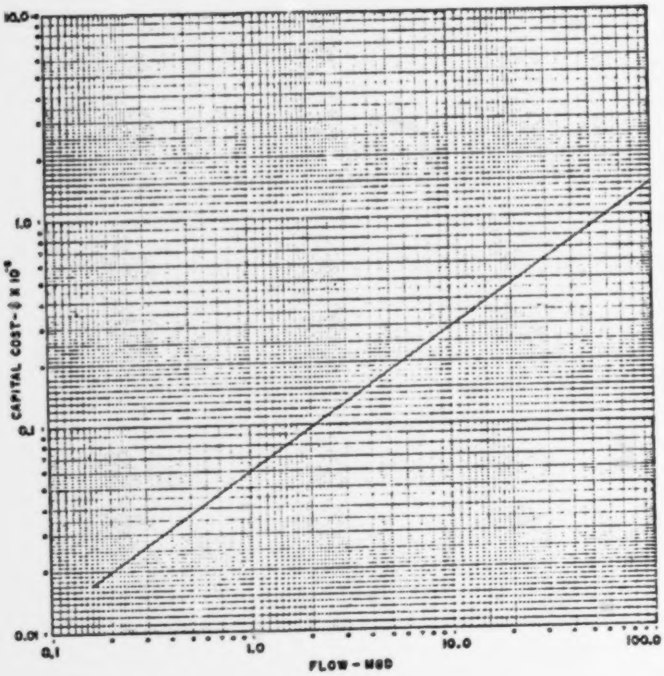


Figure B-6. Filtration capital cost relationship.

Source: DA-052

Capital Adsorption Costs (1968 dollars) - not installed

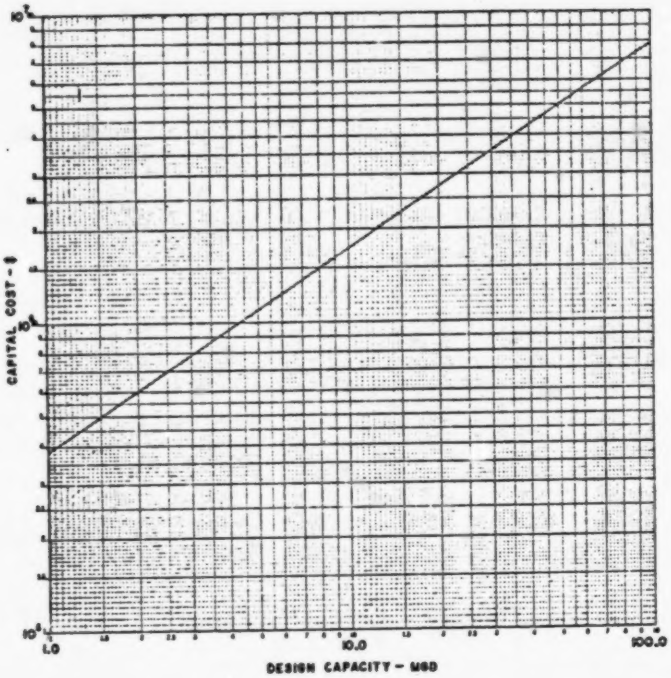


Figure B-7. Carbon adsorption capital cost relationship.

Source: DA-052

Other Process Emissions - Sludges and streams contaminated with suspended solids are generated by this system.

References - DA-052, CO-576.

FOAM FRACTIONATION

State of Development - Relatively new development, no industrial uses sited.

Applications to Date - No specific uses of this process were cited in the literature.

Process Description - Foam fractionation can be used to remove phenols from wastewater. This process involves the addition of a surfactant to the wastewater and then passing air through the mixture. The air causes the surfactant to bubble and rise to the surface. Any phenols present in the wastewater are attracted by phsycial forces to the bubbles and are carried to the surface where they are skimmed off.

Expected Performance - For an initial phenol concentration of 50 ppm foam fractionation as achieved an 85% removal efficiency.

Costs - For an initial phenol concentration of 50 ppm and an 85% removal efficiency, the cost of using foam fraction is $.09/1b. phenol. (This cost does not include cost of surfactant.)

Other Process Emissions - Aqueous stream that contains suspended solids and surfactant.

Reference - EI-026.

HIGH DENSITY SLUDGE ACID NEUTRALIZATION

State of Development - In commercial use

Application to Date - Neutralization of acid or mine waters.

Process Description - The lime neutralization of acidic and mine wastewaters results in the formation of sludges which are difficult to filter and dewater. Ground limestone avoids this problem but does not result in sufficiently high pH for effective removal of zinc and cadmium. A process which utilizes extensive recycle of sludge precipitates allows the attainment of sludges of much higher density. This allows rapid settling and eases solid-disposal problems.

Expected Performance - Results should approach those obtained with lime. Refer to summary sheet for Lime Neutralization and Precipitation.

Costs - No data available.

Other Process Emissions - Sludge

Reference - EN-394

ION EXCHANGE

State of Development - In commercial use.

Applications to Date - Ion exchange is used in many different applications today. Among its major uses is for water softening by Ca^{2+} and Mg^{2+} removals. Ion exchange is also being used for demineralizing water for high-pressure boiler systems and for chromium recovery from metals plating wastes and cooling tower blowdown.

Process Description - The ion exchange process is based on the reversible interchange of ions between a solid and a liquid phase in which there is no permanent change in the structure of the solid. Ion exchange materials are the heart of the ion exchange process. Ion exchange materials have the ability to: 1) sorb soluble ions from solutions, 2) temporarily hold these sorbed ions in chemical combination, and 3) release these ions when treated with a regenerant. The most widely used ion exchange material are resins of styrene-divinylbenzene copolymers. These resins contain functional groups which impart the actual ion exchange qualities. Sulfonic and carboxylic functional groups are employed for cation exchange resin. Conventional anion exchange resins employ amine or ammonium functional groups (ST-135).

The basic ion exchange process is the well-known two-bed demineralizer. Each bed is contained in a separate pressure vessel. The first bed consists of a cation exchange resin in the hydrogen or acid form (R-H), while the second bed consists of an anion exchange resin in the hydroxyl or base from (R-OH). The service cycle of operation achieves ion sorption by these resins. Feedwater is charged to the first resin bed containing cation exchange material. Feedwater cations are exchanged for hydrogen, i.e.

$$R\text{-}H + NaCl \rightleftarrows R\text{-}Na + HCl$$

Effluent from the cation exchanger is charged to the second bed for anion sorption. Feedwater anions are exchanged for hydroxide, i.e.

$$R\text{-}H + HCl \rightleftarrows R\text{-}Cl + HOH$$

The hydrogen and hydroxide ions introduced from cation and anion exchange, respectively, combine to form neutral demineralized water.

A degasifier is often employed to remove the soluble carbon dioxide (CO_2) in the feedwater. This CO_2 contributes to the anion content of the water which must otherwise be removed by anion exchange. Degasification is performed after cation exchange and prior to anion exchange, and it proceeds as shown.

$$H_2CO_3 \xrightarrow{\text{degasification}} H_2O + CO_2(\uparrow)$$

The quantity of CO_2 removed by degasification decreases the load on the anion exchanger by an equivalent amount.

A regeneration cycle is employed to release feedwater ions sorbed by the exchange resins and to restore these resins to their original hydrogen and hydroxide forms. Cation exchange resins are regenerated with an acid - usually sulfuric acid. Sorbed cations are eluted to the acid regenerant solution in exchange for hydrogen, i.e.

$$2(R\text{-}Na) + H_2SO_4 \rightleftarrows 2(R\text{-}H) + Na_2SO_4$$

Similarly, sorbed anions are eluted by an alkaline regeneration solution - usually caustic soda - in exchange for hydroxide, i.e.

$$R\text{-}Cl + NaOH \rightleftarrows R\text{-}OH + NaCl$$

Rinse water is used to remove excess regenerant and eluted ions from each resin bed.

Expected Performance - Ion exchange is capable of removing a number of toxic pollutants from wastewater. Cadmium has been reported to be removed to a residual level of 0.001 mg/ℓ, chromium to 0.05 mg/ℓ, copper to 0.03 mg/ℓ, cyanide to less than 0.1 mg/ℓ, lead to 0.0015 mg/ℓ, mercury to 0.005 mg/ℓ, nickel to 0 mg/ℓ, selenium to 0.001 mg/ℓ, silver to 0.001 mg/ℓ, and zinc to 0.40 mg/ℓ. Phenols reportedly are also capable of being removed effectively by ion exchange treatment.

Costs - The installed capital cost for an ion exchange system capable of removing hexavalent chromium from a cooling tower blowdown stream of 500 gpm flow is about $1.7 million. The operating and maintenance cost for this system is approximately $0.10 per 1000 gallons treated.

Those utility plant effluent streams potentially containing the pollutants removable by ion exchange include cooling tower blowdown, ash pond effluent and overflow, chemical cleaning wastes wastes, coal pile runoff, water pretreatment wastes, yard drainage, and boiler blowdown. Therefore, ion exchange could potentially be used to treat those wastes for toxic pollutant control.

Energy Requirements - The energy requirement for ion exchange treatment is for pumping. The average energy requirements is approximately 1.1 kW-hrs per 1000 gallons of water treated.

Secondary Process Emissions - The treatment of utility effluent streams by ion exchange result in resin regeneration wastes. These wastes contain the pollutants removed from the effluent stream that is treated. The pollutants are concentrated in the acidic or basic regeneration solution. The two solutions are usually combined for neutralization. Further treatment of these wastes is required prior to their discharge.

References - DI-150, MA-693, PA-120, KI-048, AV-018, ST-135.

LIME NEUTRALIZATION AND PRECIPITATION

State of Development - In commercial use

Application to Date - Presently used by itself or in conjunction with other control processes in

- wastewater treating plants,
- metal plating industry to upgrade waste effluent streams, and
- ore mining and dressing industry.

Process Description - Lime precipitation of heavy metals enjoys widespread use due to its ease of handling, economy, and effectiveness. The use of other alkaline substance is possible but lime for neutralization is the best known and studied method.

In typical lime neutralization and precipitation systems water is discharged to settling ponds to reduce the level of suspended solids. Lime is delivered as a slurry into the wastewater stream in the primary or in secondary settling ponds. A pH level of about 9 is usually needed to remove most heavy metals. A pH of 10-12 may be necessary in some cases. The attached table illustrates pH levels required.

Expected Performance - Among the metals effectively removed at basic pH are: As, Cd, Cu, Cr^{+3}, Fe, Mn, Ni, Pb, and Zn. Based on published sources, industry data, and analysis of samples, it appears that the concentrations given below may be routinely and reliably attained by hydroxide precipitation in the ferroalloy-ore mining and milling industry (EN-394).

TABLE B-7. CONCENTRATIONS OF HEAVY METALS AFTER HYDROXIDE PRECIPITATION

Metal	Concentration (mg/ℓ)	Metal	Concentration (mg/ℓ)
As	0.05	Mn	1.0
Cd	0.05	Ni	0.05
Cu	0.03	Pb	0.10
Cr^{+3}	0.05	Zn	0.15
Fe	1.0		

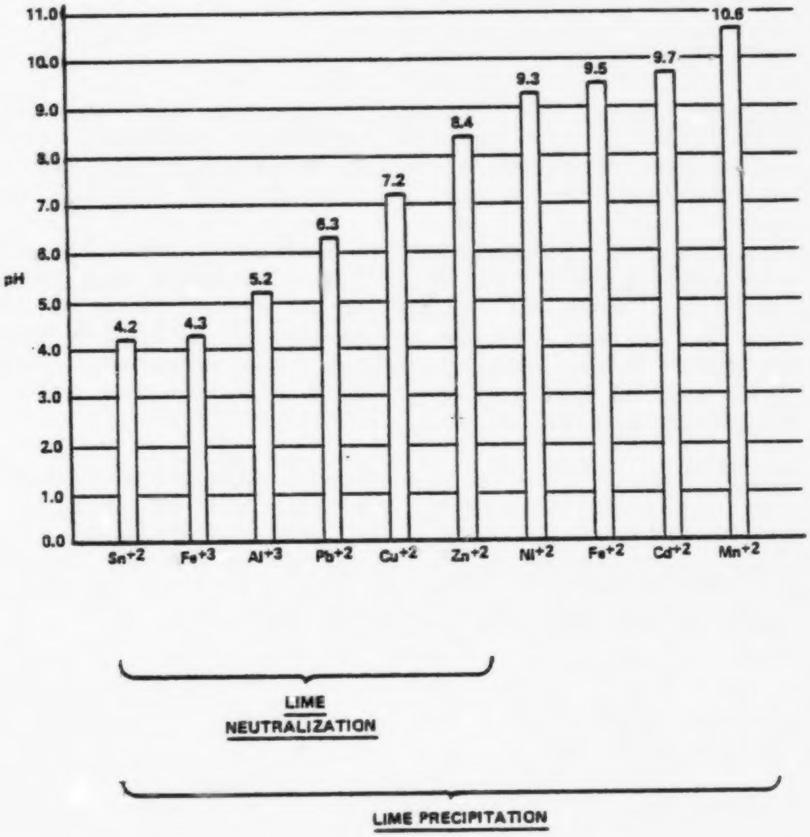


Figure B-8. Minimum pH values for complete precipitation of metal ions as hydroxides.

Some results of lime precipitation reported for the Cu, Zn, and Pb smelter industries are given below in ppm:

TABLE B-8. HEAVY METAL CONCENTRATIONS AFTER LIME PRECIPITATION

Metal	Cu Smelter	Zn Smelter	Pb Smelter
Cd	0.6	0.02	0.7
Pb	0.19	0.15	2.7
Hg	0.0001	0.004	0.009
Zn	18.9	50.0	1.2

Figure B-9 reflects the experience gained from a zinc plant/lead smelter.

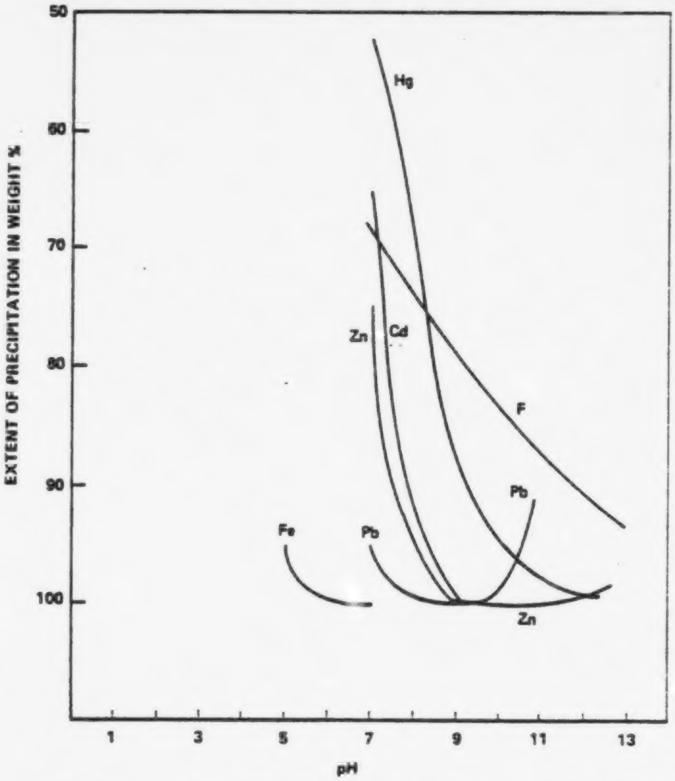


Figure B-9. Heavy metal precipitation vs. pH for tailing-pond effluent pH adjustments by lime addition.

Costs - The costs for treating 545 cu. m/day (100 gpm) of process wastewaters prior to release to navigable waters by lime and settling are estimated (EN-391) as follows:

- Capital Costs (1971 dollars)

  Lime and settle treatment plant ($150,000)

- Operating Costs ($/year)

  Operating and maintenance ($53,200)

Other Process Emissions - A metal hydroxide sludge is produced which must be periodically removed from settling ponds.

References - EN-391, EN-392, EN-393, EN-394.

LIQUID WASTE INCINERATION

State of Development - In commercial use.

Applications to Date - Liquid waste incineration is used for chemical plant and refinery cleaning operations when the cleaning residues are not recovered for economic reasons. Numerous other applications are found where disposal of liquid organic compounds is necessary.

Process Description - In order that a liquid waste may be considered combustible, there are several rules of thumb which should be used. The waste should be pumpable at ambient temperatures or capable of being pumped after heating to some reasonable temperature level. The liquid must be capable of being atomized under these conditions. If it cannot be pumped or atomized, it cannot be burned as a liquid but must be handled as a sludge or solid. Liquid waste incineration generally involves liquids having viscosities up to approximately 1,000 SSU, although lower viscosities are desirable.

In order to be considered a combustible liquid waste, the material must sustain or support combustion in air without the assistance of an auxiliary fuel. This means that the waste will generally have a calorific value of 8,000 to 10,000 Btu/lb or higher. Below this calorific value, the material would not exhibit properties which would enable it to maintain a stable flame in a commercial combustor or burner. Materials which fall into this category (>8,000 Btu/lb) are light solvents (such as toluene, benzene, acetone, ethyl alcohol) and heavy organic tars and still bottoms similar to residual fuel oil. The wastes may be combinations of both, which would give a mixture having an intermediate viscosity and heating value. These wastes come from cleaning operations in chemical plants and refineries or are the residues from distillation processes and are usually not recovered for economic reasons.

The equipment which is used to incinerate combustible liquid waste can also vary from manufacturer, but its basic form will be that of a combustor or burner designed to handle a liquid waste through a steam, air, or mechanical atomizing nozzle. High heat release combustors require minimal secondary incineration chambers, but usually incineration is carried out in combustion chambers having volumes which provide for a heat release of 25,000 Btu/hr-cu. ft. of combustion volume. Residence times within an incinerator burning liquid waste will vary from 0.5 to 1 sec. The combustion chamber is usually cylindrical in shape and may be used in a vertical or horizontal arrangement. The vertical chamber has the advantage that the incinerator acts as its own stack, but obviously it is not well adapted to a tall stack arrangement. Horizontal incinerators can be more easily connected to tall chimneys or stacks. Some specially designed rotary kilns have been applied to the disposal of liquid chemical warfare agents.

Expected Performance - Incineration of the liquid cleaning wastes from utility equipment would result in effectively 100% removal by disposal of the organics before they are discharged to the plant sewer system.

Costs - H.F. Lund reports the equipment cost for incinerators handling combustible liquid wastes to be about $200-350 per gallon/hr capacity.

Other Process Emissions - If the waste stream contains inorganic salts, halogen compounds, or sulfur compounds an air pollution problem will result. Incinerator ash constitutes a small solid waste stream.

References - AZ-009, LU-013, OT-029.

CHEMICAL REDUCTION

State of Development - In commercial use

Applications to Date - Chemical reduction is commonly used to remove chromium by reduction of hexavalent chromium to the trivalent ion. Trivalent chromium is then removed by chemical precipitation. Variations of processes to reduce hexavalent chromium find use in metal finishing, electroplating and utility industries.

Process Description - The chemical reduction of hexavalent chromium is carried out by adjusting the pH to about 3 followed by the addition of a reducing agent such as sulfur dioxide. The trivalent chromium produced is then precipitated by lime addition at a pH of about 9.

Typical chemical reactions are:

$$2H_2CrO_4 + 3SO_2 \rightarrow Cr_2(SO_4)_3 + 2H_2O$$

$$Cr_2(SO_4)_3 + 3Na_2CO_3 + 2H_2O \rightarrow Cr_2(OH)_4CO_3\downarrow + 3Na_2SO_4 + 2CO_2\uparrow$$

$$2Na_2CrO_4 + 3Na_2S_2O_4 + Na_2CO_3 + 2H_2O \rightarrow Cr_2(OH)_4CO_3\downarrow + 6Na_2SO_3$$

The reduction of Cr^{+6} with SO_2 can be carried out on highly concentrated streams and is operated at low pH. The reactions with sodium carbonate and sodium hydrosulfite result in both neutralization and reduction. The treatment levels for use of SO_2 with chromium plating and etching wastes is 1,000-2,500 mg SO_2/ℓ and for sodium carbonate - sodium hydrosulfite is 200-500 mg $Na_2S_2O_4/\ell$ and sufficient Na_2CO_3 to provide a pH of about 8.

Expected Performance - Reported effluent levels vary from "zero" to 1 mg/ℓ. Typical results for chromium are 0.02 mg/ℓ Cr^{+6} and 0.01 mg/ℓ Cr^{+3}. The neutralization of streams after hexavalent chromium reduction will result in the precipitation of Sn, Fe, Al, Pb, Cu, Zn, Ni, Cd, Mn, etc. The effectiveness of neutralization on removal of metals as hydroxides is pH dependent.

Costs - The use of bisulfite as the reducing agent and caustic soda to adjust pH costs about $0.50 per pound of chromium assuming 6.5¢/lb of caustic and 11.5¢/lb of sodium bisulfite.

Other Process Emissions - If the chemical reduction step is followed by neutralization or alkaline pH adjustment, a metal hydroxide sludge will result.

References - WI-260, SM-159, EN-127, EN-394.

PHOTOCHEMICAL OXIDATION

State of Development - Presently only a laboratory experiment.

Application to Date - No industrial applications for this process are known.

Process Description - Phenol solutions which are exposed to light will also degrade by an oxidative mechanism. Exposure to sunlight or aritficial light leads to the consumption of oxygen and the conversion of the phenol to low molecular weight acids, carbon dioxide and water. Similarly, flash photolysis of phenol solutions will lead to their oxidative degradation by a free radical mechanism.

Expected Performance - For an initial phenol concentration of 5400 ppm, photochemical oxidation has attained a phenol removal efficiency of 70%.

Costs - For an initial phenol concentration of 5400 ppm and a 70% removal efficiency, the treating costs of photochemical oxidation are $0.22-0.26/lb phenol (not including pretreatment costs).

Other Process Emissions - None are expected.

Reference - EI-026

REVERSE OSMOSIS

State of Development - Commercially available.

Application to Date - Limited use in the electric utility industry.

Process Description - Desalination of water is accomplished by pumping through a membrane at high pressure (~400 psi). Pretreatment of the inlet water is required.

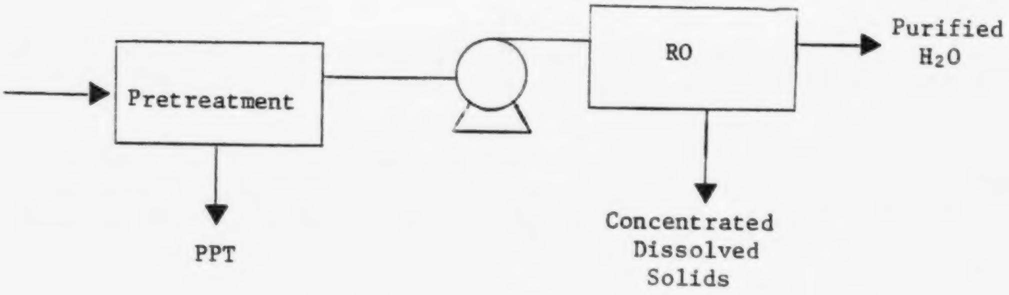


Figure B-10. Flowsheet for reverse osmosis.

Expected Performance - >90% removal for dissolved solids
>95% organics

Costs - Capital costs \$1/gal/day. O/M costs (including membrane replacement) = \$0.75/1000 gal.

Energy Requirements - Pumping costs

Other Process Emissions - PPT from pretreatment, concentrated dissolved solids stream from RO section

References - Vendor contract - Hydranautics

SKIMMING AND FLOTATION

State of Development - In commercial use

Application to Date - Removal of oil from wastewater.

Process Description - Oil is generally removed from wastewater by passing the water through a lagoon or through a series of inverted weirs; the oil floats to the top and is skimmed off. Granular absorbents may be used to assist in the collection and removal of the oil. Air flotation can also be used to aid in the agglomeration and separation of the oil phase.

Expected Performance - Removal of oil to form an oil concentrate. Specific residual level not known.

Costs - No data available.

Other Process Emissions - Oil concentrate

References - EN-392

SOLVENT EXTRACTION

State of Development - Developmental

Applications to Date - Solvent extraction has not been applied to wastewater treatment on a commercial scale. It is used primarily for separating mixtures of liquids. In the petroleum refining-petrochemical industries solvent extractions is used in numerous processing steps and in the minerals processing industry it is used for the separation of uranium from vanadium in ore-leach liquors. Currently, few extraction processes involve separation from water, and almost none involve water as the major phase.

Process Description - Fundamentally, solvent (liquid) extraction involves the separation of components of a solution. The separation requires that the components have different relative solubilities in two immiscible, or only partially miscible liquid solvents.

The extraction is accomplished by passing two phases countercurrent to each other. This is done on a multistage contactor which may be considered to be divided into two parts, the extraction section and the scrubbing section. The aqueous or original solution is usually fed into the contactor near its middle. The solvent is introduced at one end of the extraction section through which it flows countercurrent to the aqueous feed. The extraction section is so-called since it is here the desired component of the aqueous feed (the solute) is extracted. The purpose of the scrubbing section is to provide a means to wash the solvent leaving the extraction section to remove any undesirable solutes.

After the solvent has exited the contactor the final process step involves separating the solute from the solvent. The regeneration depends upon whether the original extraction involved interaction between the solvent and solutes or whether the extraction depended only on physical effects. In the latter case, distillation is by far the most common means of regeneration. In the other case, regeneration involves reversal of the solvent/solute interaction which is usually done by chemical conditioning.

Expected Performance - No data were found discussing the removal effectiveness of solvent extraction for toxic pollutant control.

Costs - No economic information was found on solvent extraction applied to wastewater treatment.

Energy Requirements - No information.

Other Process Emissions - Intimate contact between the solvent and wastewater stream being treated could result in carryover of some of the solvent in the wastewater discharge. Further treatment would then be necessary for solvent removal.

References - MA-246

SULFIDE PRECIPITATION FOR REMOVAL OF HEAVY METALS

State of Development - This process is commercially available and used.

Application to Date - This process has been used to control mining and milling wastewaters.

Process Description - This process accomplishes more complete removal of heavy metals than the use of hydroxide for precipitation. The treatment of wastewater with either sodium sulfide or H_2S can effectively remove Cd, Cu, Co, Fe, Hg, Mn, Ni, Pb, Zn, and other metals. On the whole, this process removes both heavy metals and some sulfur from waste streams but requires some energy expenditure (it involves an energy loss in the partial oxidation of carbon).

In practice, this technique can only be applied when the pH is sufficiently high (>8) to assure generation of sulfide ion rather than bisulfide or H_2S. Because of the toxicity of the sulfide ion and H_2S, the case of this process may require both pre- and post-treatment and close control of reagent additions. Pretreatment involves raising the pH of the waste stream to minimize the evolution of H_2S.

Expected Performance - The following control effectiveness was exhibited in a chlor-alkali plant:

	Removal Range	Avg. Removal
Hg	87-99%	97%

Comment: Hg present in conc. 10-100 ppm.

For use in the utility industry, this control process should be suitable for application to:

- and pond effluent,
- cooling tower blowdown, and
- yard drainage.

Costs - For chlor-alkali plant:

- Cap. cost = $143,000
- Oper. cost = 50¢/1000 gal.

Other Process Emissions - A metal-sulfide sludge is produced by this process.

References - EN-391, EN-394.

ULTRAFILTRATION

State of Development - In commercial use in the petrochemical, refining and mining industries.

Applications to Date - Ultrafiltration has been applied on a sig significant commercial scale to the removal of oil from oil emulsion, yielding a highly purified water effluent and an oil residue sufficiently concentrated to allow reuse, reclamation, or combustion.

Process Description - This process is similar to reverse osmosis in that pressure is used to force water through semi-permeable membranes. Ultrafiltration retains materials of 500 or greater molecular weight. Pressures of 259 to 517 cm of Hg are generally used.

Equipment is readily available, and present-day membranes are tolerant of a broad pH range. Use of ultrafiltration in mining and milling may provide a means for removing high levels of oils used in flotation.

Expected Performance - Retain materials of molecular weight of 500 or greater.

Costs - No data available.

Other Process Emissions - Oil or concentrated residue.

References - EN-394.

ULTRASONIC OXIDATION

State of Development - Presently experimental.

Applications to Date - Since this process is experimental, the practical aspects of this process have not yet been exploited.

Process Description - When phenol solutions are subjected to an ultrasonic field in the range 800-1000 kc/sec for up to two hours, the phenol is oxidized in turn to hydroxylated intermediates, quinones, aliphatic acids and carbon dioxide. The rate of oxidation increases with the intensity of the ultrasonic field and is practically independent of pH in the range 3-9.

Expected Performance - For an initial phenol concentration of 50 ppm, ultrasonic has exhibited a 100% removal efficiency.

Costs - No treating cost information is available.

Other Process Emissions - None are expected.

Reference - EI-026.

ZERO DISCHARGE

State of Development - Components are all commercially available.

Applications to Date - Several power plants have implemented this technology.

Process Description - No water discharges from the power plant. Water reuse/recycle management combined and/or water purification step can be used to eliminate water discharges.

Flow Sheet - There are various site-specific flow schemes for implementing zero discharge. Detailed flow diagrams for the major methods of obtaining zero discharge are listed in the detailed analysis of zero discharge.

Expected Performance - Complete recycle of liquid.

Costs - For a zero discharge system using a brine concentrator:

Capital investment - $10/gpd

O/M - $2.00/1000 gal

Energy Requirements - Dependent upon which type system used.

References - EN-127, RI-160.